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Pilot Anaerobic Biological Treatment of Pulp Mill Evaporator Foul Condensate

HydroQual, Inc., Mahwah, NJ

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PILOT ANAEROBIC BIOLOGICAL TREATMENT OF PULP MILL EVAPORATOR FOUL CONDENSATE

by

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Contract No. 68-03-3074

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The performance of three new anaerobic biological treatment technologies were compared and evaluated. Data were obtained from the operation of pilot plants representative of the anaerobic filter, anaerobic upflow sludge bed, and anaerobic fluidized bed. A review of recent literature presents information on these technologies developed in laboratory, pilot-scale and full-scale plants. The wastewater selected for this study was the evaporator foul condensate from an ammonia-based sulfite pulping mill at Procter and Gamble's Mehoopany, Pennsylvania plant. During pilot plant construction, laboratory screening studies were conducted to determine wastewater characteristics and anaerobic treatability.

The pilot plants were operated for seven months. Results indicated that the anaerobic fluidized bed performance was excellent, achieving high COD removals of 70 to 90 percent at reactor volumetric loadings from 7 to 100 kg/m^3-day. The anaerobic filter achieved 70 to 80 percent COD removals at loadings of 6 to 25 kg/m^3-day. The anaerobic upflow sludge bed required external clarification and sludge return to retain solids in the system; loadings of about 5 kg/m^3-day with COD removal of 80 to 90 percent were attained by the end of the study.

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FOREWORD

The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water systems. Under a mandate of national environmental laws, the agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. The Clean Water Act, the Safe Drinking Water Act, and the Toxics Substances Control Act are three of the major congressional laws that provide the framework for restoring and maintaining the integrity of our Nation's water, for preserving and enhancing the water we drink, and for protecting the environment from toxic substances. These laws direct the EPA to perform research to define our environmental problems, measure the impacts, and search for solutions.

The Water Engineering Research Laboratory is that component of EPA's Research and Development program concerned with preventing, treating, and managing municipal and industrial wastewater discharges; establishing practices to control and remove contaminants from drinking water and to prevent its deterioration during storage and distribution; and assessing the nature and controllability of releases of toxic substances to the air, water, and land from manufacturing processes and subsequent product uses. This publication is one of the products of that research and provides a vital communication link between the researcher and the user community.

This report presents the results of a research program which has provided information on the operation and performance of pilot plants on three new, emerging, anaerobic treatment technologies, particularly applicable to high strength wastewaters. The results of the project illustrate the applicability of the technologies to the wastewater studied and their potential for treatment of other wastewaters. Performance and design data generated in this study should provide informative and useful information to potential users of these technologies.

Francis T. Mayo, Director
Water Engineering Research
Laboratory

ABSTRACT

The performance of three new anaerobic biological treatment technologies were compared and evaluated. Data were obtained from the operation of pilot plants representative of the anaerobic filter, anaerobic upflow sludge bed, and anaerobic fluidized bed. A review of recent literature presents information on these technologies developed in laboratory, pilot-scale and full-scale plants. The wastewater selected for this study was the evaporator foul condensate from an ammonia-based sulfite pulping mill at Procter and Gamble's Mehoopany, Pennsylvania plant. During pilot plant construction, laboratory screening studies were conducted to determine wastewater characteristics and anaerobic treatability.

The pilot plants were operated for seven months. Results indicated that the anaerobic fluidized bed performance was excellent, achieving high COD removals of 70 to 90 percent at reactor volumetric loadings from 7 to 100 kg/m^3-day. The anaerobic filter achieved 70 to 80 percent COD removals at loadings of 6 to 25 kg/m^3-day. The anaerobic upflow sludge bed required external clarification and sludge return to retain solids in the system; loadings of about 5 kg/m^3-day with COD removals of 80 to 90 percent were attained by the end of the study.

An analysis of COD removal per unit of volatile suspended solids per day, showed within the scatter of data collected, that there was no significant difference in removal rate, based on food to microorganism loading, among the three pilot systems. The volumetric loading capacity developed in each system over the study period was related to the ability of the processes to retain biological solids. Though longer operation of the systems may have resulted in development of greater volumetric loading

capacities, particularly for the upflow bed and anaerobic filter, the results of this study clearly indicated significant differences in loading capacity during startup and several months of initial operation.

Volume 2, the appendices to this report, contains quality assurance and control data, Procter and Gamble report on the operation of the anaerobic acclimator, the screening study data, and the pilot plant data.

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LIST OF ABBREVIATIONS AND SYMBOLS

Abbreviations

VA = Volatile acids as acetic acid
HA_C = Acetic acid
COD, COD_T = Total chemical oxygen demand
COD_F = Chemical oxygen demand, filtered sample
BOD_F = Biochemical oxygen demand, filtered sample, (5 day)
BOD, BOD_T = Total biochemical oxygen demand, (5 day)
TOC = Total organic carbon (all TOC analyses on filtered samples)
COD_R = Removed; based on total influent, filtered effluent sample
BOD_R = Removed; based on filtered influent, filtered effluent sample
TOC_R = Removed; based on total influent, filtered effluent sample
TS = Total solids
TDS = Total dissolved solids
TVS = Total volatile solids
SS = Suspended solids
VSS = Volatile suspended solids
MLSS = Mixed liquor suspended solids
NaOH = Caustic, sodium hydroxide
$CaCO_3$ = Lime as calcium carbonate
NH_3Cl = Ammonium chloride
K_2HPO_4 = Potassium monophosphate
SO_4 = Sulfate
SO_3 = Sulfite
S = Sulfide
PO_4-P = Phosphate as P
TKN = Total Kjeldahl nitrogen as N
NH_3-N = Ammonia nitrogen as N

Color PCU = Color measured in platinum cobalt units

Na = Sodium

K = Potassium

Ca = Calcium

Mg = Magnesium

Ni = Nickel

Zn = Zinc

Co = Cobalt

Se = Selenium

Cr = Chrome

Cu = Copper

Fe = Iron

As = Arsenic

mg = milligram

g = gram

kg = kilogram

ml = milliliter

l = liter

mm = millimeter

cm = centimeter

m = meter

hr = hr

d = day

kg/m^3-d = kilograms per cubic meter of reactor volume per day

USEPA = United States Environmental Protection Agency

UASB = Upflow Anaerobic Sludge Blanket

S_T = Total soluble COD concentration

V_1 = Liquid volume in bed

X = Total mass of biological (volatile) solids in bed

h = Fluidized bed height

h_1 = Sludge sand interface

Q_i = Influent flow

Q_R = Recycle flow

G = Gas

t_o = Hydraulic detention time

R_T = Soluble COD removal rate

Sc = Complex organic COD

Svc = Combined complex and volatile acid COD

Xc = Volatile acid formers

Xv = Methane formers

CH_3-COOH = Acetic acid

Rc = Complex COD removal rate

Rv = Volatile acid removal rate

Rxc = First stage reaction rate

Yc = Yield coefficient acid formers

Yv = Yield coefficient methane formers

μ_v = Maximum net growth rate of methane formers

t = Time

k_v = μ_v/Y_v

K_s = Michaelis constant

S = Substrate concentration

R = Substrate removal rate

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Key personnel participating in the project included Eugene J. Donovan, Jr., Project Director, Thomas J. Mulligan and James A. Mueller, Project Technical Review, K. Subburamu, [illegible]neer, Richard Scheible, Director of Laboratories and Quality Assurance Officer, and John Leavy, Chemist. Special acknowldgement is made of the efforts of Karen Klein, word processing, and Joseph McDonald, drafting.

IT Corporation was responsible for the detailed design and construction of the pilot plants. Personnel involved in contract management and in providing assistance in setting up and relocating the pilot plants include Jurgen Exner, Director, James Blackburn, Project Manager, and Edward Alperin, Engineer.

The cooperation and assistance of the Procter and Gamble Paper Products Company is appreciated. Procter and Gamble provided the site for the pilot plant location, waste, and required utilities. Their personnel operated the preacclimation system, assisted in maintaining the pilot plant equipment, and made pertinent comments on the study program and results. Key personnel included Donald Hahn, Gary Johnson, William Eberhart, Dale Kryzinski, and Stan Lane.

SECTION 1

INTRODUCTION

OBJECTIVES

This study included the design and construction of three pilot plants representative of relatively new and innovative anaerobic processes. These plants were to be used to study anaerobic treatment of industrial wastes. An initial, limited pilot plant program was conducted using the pilot plants to gain experience in their operation and to evaluate and demonstrate their performance on a high strength industrial wastewater.

The objectives included the development of operating and treatment design parameters appropriate to each process; an assessment of the applicability of the processes to various industrial wastewater classifications based on existing information and study results; and development of a final report to present the results of the study. Three anaerobic systems selected for this study included (a) upflow sludge blanket, (b) filter, and (c) fluidized bed.

Conclusions and recommendations from this study are presented in Section 2. The project included a review of current literature on anaerobic treatment technologies which is summarized in Section 3 of this report. Section 4 presents the results of the preliminary waste characterization and laboratory screening studies of anaerobic treatment of the waste. The pilot plant facilities are described in Section 5, and Section 6 describes the pilot plant study plan and quality assurance program. Pilot plant results are presented in Sections 7 and 8.

BACKGROUND

Anaerobic biological treatment of industrial wastewaters is becoming more relevant because of potential cost advantages over historically applied aerobic biological treatment systems. Anaerobic treatment has two major advantages over aerobic treatment: (1) an energy surplus is typically produced in the form of methane gas, and (2) significantly fewer solids are produced for ultimate disposal. These two advantages alone can result in significant operating cost differentials between aerobic and anaerobic treatment, particularly for high-strength wastes. These factors have stimulated extensive interest in applying anaerobic pretreatment to industrial high strength wastewaters.

Conventional anaerobic digestion, extensively used at wastewater treatment plants,(2) and at animal and meat processing plants,(3) has not been found to be cost competitive with aerobic (activated sludge) treatment for soluble organic wastewaters, because of the signficantly longer detention times required to achieve organic reduction.(4) To decrease the required size of the anaerobic reactors, approaches similar to the aerobic activated sludge process were initially developed in which active microorganisms were settled from the reactor effluent and returned.(1,4,5) In addition, fixed film processes have been developed in which biological growth is retained in the reactor as the waste passes through.(1,4,5) Various concepts have been studied on laboratory and pilot scales and several have been commercially developed and applied in full-scale to a limited number of industrial wastes. All appear to have favorable economic advantages compared with aerobic treatment, even at the lower ranges of loading reported. Wide variations exist in design loadings, performance, and applicability to various wastestreams, and there is a need for ongoing evaluations of the various types of anaerobic treatment systems, engineering designs, applicability to specific industrial wastes, and economics and performance of various systems.

The more prevalent of the new anaerobic treatment systems include the anaerobic suspended growth sludge recycle system, the anaerobic upflow sludge blanket system, the anaerobic filter and the anaerobic fluidized bed. Studies to evaluate such processes are needed because of their potential economic advantages, heightened interest, considerable range of appplications, and the need for information other than that provided by commercial interests.

PROJECT LOCATION--PLANT SITE

A selection was made to conduct this study with the foul condensate wastestream from a multi-stage evaporator that processed ammonia-based spent sulfite liquor at the Procter and Gamble Paper Products Company, Mehoopany, Pennsylvania. The waste was known to be biologically degradable, had a high strength (9,000 to 10,000 mg/l BOD), constituted about 50 percent of the plant's waste BOD load, and was a likely candidate for anaerobic treatment. Procter and Gamble was very interested in the project and agreed to cooperate and assist in the study. Procter and Gamble provided an indoor location for the pilot plants and an adjacent site for a mobile laboratory that was built for this study. All required utilities were provided at the site, including electric, light, water, foul condensate cooling, and wastewater piping to the pilot units. Procter and Gamble personnel also assisted in setting up and maintaining the pilot plants.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

The study met the project objective of building and operating three new, innovative anaerobic process pilot plants to compare their performance using an industrial wastewater that would be a good candidate for anaerobic treatment. This limited 7-month pilot study demonstrated the utility of the pilot plants for studying each process and developing treatability and design data.

Laboratory screening studies (conducted before the pilot plant testing) on the foul condensate wastewater provided useful information relating to degradability, toxicity, neutralization requirements and start up procedures for the pilot plant system. After neutralization of the waste and acclimation of an anaerobic sludge obtained from a municipal digester, the bench studies demonstrated that the waste was readily degraded by anaerobic treatment.

Start up of the anaerobic pilot plants was accomplished within 15 to 20 days by recycling full-strengh waste (10 to 15 g/l COD) after adding acclimated sludge and biologically coated media to the upflow sludge blanket and both fixed film pilot plants, respectively.

The anaerobic upflow sludge blanket, anaerobic filter and anaerobic fluidized bed pilot plants were operated, and data were collected on loading and COD removal. Loading rate goals on the anaerobic filter of 6 to 30 kg COD/m^3-d were met. Similar fluidized bed loading goals were substantially exceeded with loading for a short period exceeding 100 kg COD/m^3-d. Loading rate goals for the upflow sludge blanket were met only at the lower range of 6 kg COD/m^3-d; increased loading capacity could not be developed on this pilot plant during the study period. Quality control goals and objectives for the data collection and sampling program were met in the project.

Steady-state conditions can be a misleading description for anaerobic processes, since these systems are dynamic, with biological growth rates responding to loadings, and retention of new growth depending on the type of system, and other biological and physical factors at any given time and loading level. In this study, steady-state conditions were defined as constant removal at constant loading. Though a range of removals and loading conditions were measured, relatively steady-state conditions were achieved at various organic loading levels on the pilot plants. Attainment of steady-state was related to each system's ability to retain biological growth.

Rapid buildup of a sludge zone in the fluidized bed resulted in attaining relatively steady-state conditions rather quickly. On the other hand, the upflow sludge blanket system evidenced a loss of biological solids without an external clarifier, and a very slow buildup of removal capacity with an external clarifier. The filter gradually and continually developed removal capacity throughout the study as solids grew on the media. Complete steady-state conditions were probably never attained in the pilot units; however, the data analyzed were reasonably representative of each system's performance at various loading levels achieved over varying periods of time.

Gas production based on COD removal was similar in all three systems. Approximately 0.4 to 0.5 m^3 of gas was produced per kg of COD removed. The gas contained an average methane content of 68 percent. Methane concentration in the gas was a function of the pH maintained in the reactor and varied from 55 to 80 percent as pH varied from 6.5 to 7.8. Partial conversion of sulfate and sulfite in the waste to hydrogen sulfide occurred in the systems. The gas contained 0.5 to 2 percent hydrogen sulfide.

Effluent recycle for all three units, along with gasification, resulted in rapid mixing of the influent throughout the reactor volume. Effluent recirculation enhanced utilization of the full reactor volume, and minimized organic concentration in the inlet zone, thus avoided depressed pH levels in the zone, and aided temperature control in the reactor during periods of no waste flow.

Solids distribution in the reactors was measured. The majority of biological solids accumulation in the fluidized bed reactor occurred in a zone above the media zone. This sludge zone contained a minimal amount of media and about 3 percent volatile solids. The lower media zone contained very few volatile solids (less than 3000 mg/l). Based on this observation it was concluded that the amount of media in the fluidized bed could be significantly reduced to the extent required for bed support, recycle liquid distribution, and for weighting biological solids in the sludge zone. Reduction in bed volume could reduce the total volume required in the reactor, reducing its cost, would permit higher unit volumetric loading rates, and possibly reduce recycle requirements.

Attached biological solids were found on the media throughout the full depth of the anaerobic filter. Higher concentrations of attached and suspended solids were found in the lower part of the filter. A special study indicated that approximately equal COD removal rates occurred in the top and bottom halves of the filter, indicating full use of the media and justification of scale-up to full size units at greater depths.

Solids development in the upflow sludge bed unit was very slow. Most of the original seed sludge (about half the reactor volume at 3 percent solids) was washed out during operations without an external clarifier. More than 60 percent of the final sludge accumulation was found in the bottom 3 to 4 percent of the reactor volume at the end of the study. Assuming the possible eventual accumulation of settleable sludge in a greater portion of the reactor, it was concluded that a substantial potential for much greater volumetric removal capacity existed in the upflow bed unit. Long-term studies would be required, however, to confirm and demonstrate this potential.

A simplified kinetic analysis of the fluidized bed system, which was operated over a wide range of loadings, provided a basis for understanding the system. The analyses, using Michaelis kinetics, indicated a maximum methane-forming organism growth rate, within 25 percent of that found in suspended growth anaerobic systems. The Michaelis half rate constant determined from the data, was significantly greater than literature values and indicated that a volatile acid concentration of approximately 2500 mg/l was required to maintain reaction rates at 80 percent of the maximum rate. This result is significant in determining operating conditions to develop growth and removal capacity.

An analysis of wastewater feed COD removed per unit of volatile suspended solids as a function of total soluble COD concentration showed, within the scatter of data collected, that there was no significant difference in the removal rate among the three pilot systems.

Operation of the systems on recycle only for several days without any waste feed indicated that the maximum COD removals obtainable were about 89 to 93 percent. Volatile acid concentrations measured were in the range of 300 to 600 mg/l under no load conditions. Typically, low-load anaerobic systems reduce volatile acids below 50 to 100 mg/l.(2) The reason for the relatively high volatile acids was not apparent.

After several months of operation, suspended solids settling tests on the filter effluent indicated about 9 percent settleable solids remained in the effluent from the unit, and on the upflow sludge blanket reactor effluent, about 74 percent of the effluent solids were settleable in 3 hours. There was wide scatter of the data on suspended solids settleability.

RECOMMENDATIONS

In general, further research and demonstration studies should be done using pilot plants to determine anaerobic treatment applicability to industrial wastewaters with a variety of characteristics. Each of the processes may have specific advantages for specific types of waste.

Continuing development of processes and engineering designs of anaerobic technology is currently needed and recommended. Although anaerobic systems have been subjected to laboratory and pilot-scale tests, further research is needed to obtain a better understanding of the anaerobic process, particularly as related to specific wastewaters.

Further research is recommended on the biochemistry of anaerobic digestion and the factors included in the formation of the granular type of settleable sludge reported in the upflow sludge blanket systems on certain food industry wastes.

Further engineering development is needed for the fluidized bed system with respect to type and quantity of media and recycle distribution. Concern has been expressed over the potential for buildup of solids and eventual clogging of the anaerobic filter. Systems of this type should include waste and gas recycle to control potential clogging and a long-term evaluation of the operating systems should be conducted to evaluate the potential clogging problem.

Further development should be undertaken to determine anaerobic system kinetics and long-term performance of all three systems under design loading conditions with typical industrial wastes, either on a pilot- or full-scale basis. These studies are needed to substantiate loading versus removal relationships for specific wastes and system designs, and to instill greater confidence in the engineering community with respect to the feasibility and long-term viability of high-rate anaerobic treatment processes.

To expand the potential applications of these technologies, emphasis should be placed on the effect and applicability of the processes at lower temperatures and lower organic concentrations.

SECTION 3

LITERATURE REVIEW

GENERAL REVIEW

Information was reviewed on the anaerobic treatment technologies to be studied in this project. Currently, widespread interest exists in the application of anaerobic treatment to strong industrial wastewaters because of the potential economic favorability. A significant amount of research and published information has appeared, particularly in the last five years, describing both the biotechnology involved and applications of anaerobic waste treatment in laboratory units, pilot plants, and commercialized plants.

The basic concept involved in these newly developed and developing systems is the retention of the anaerobic microorganisms. This permits relatively high loading rates and shorter wastewater retention times in the systems, than conventional anaerobic systems used for sludges at domestic wastewater treatment plants. The obvious results are smaller systems (lower capital costs) and the ability to anaerobically treat soluble organics in the wastestream.

Although it is recognized that new information is being continually developed, this review is primarily intended as an overview of recent information on the three types of systems studied in this project: (a) the anaerobic upflow sludge bed, with and without external clarification, (b) the submerged fixed media system (anaerobic filter), and (c) the fluidized media system (upflow fluidized bed). Several excellent reviews(1,2,3,4) of the application of anaerobic technology utilizing these new systems to industrial wastewaters have been published.

Dague's review(1) traces research conducted on the anaerobic filter which originated with work conducted by Young and McCarty in 1967 on laboratory rock media filters using synthetic waste, to recent full scale anerobic filter systems.

Sheridan(2) in 1982, presented a brief history of anaerobic technology from 1776 with the discovery of methane production in swamps, to current day, full scale systems; the anaerobic suspended growth contact system, 1959 and 1972; anaerobic filter 1969 and 1977; sludge blanket 1977; and fluidized bed 1982. He also summarized information and data on the three full scale anaerobic filters commercialized as the Celrobic® process by the Celanese Chemical Company. He provided an economic comparison of aerobic and anaerobic systems, indicating an energy cost favorability in 1982, for anaerobic treatment of \$120/ton COD removed, using a power cost of \$.05/kwh. An analysis, including capital and operating costs of the anaerobic filter system, indicated that favorable economics for anaerobic systems depend on both wastewater flow and waste strength. Small volume, high strength wastes; (0.1 mgd, > 5,000 mg/l COD), and large volume, moderate strength wastes; (1.0 mgd, > 2,000 mg/l COD) were found to be the limits for a preliminary assessment of the applicability of anaerobic filter treatment.

Olthof(3) in 1982 presented a review and provided a few examples of full scale anaerobic treatment plants on industrial wastes. He compared the advantages and disadvantages of anaerobic versus aerobic treatment, and those of several types of anaerobic reactor systems. An example of economics indicated an operating differential of \$179 per 1,000 kg COD, in favor of anaerobic treatment over aerobic processes.

Speece(4) presented an overview of the scientific principles and technological concepts of anaerobic biotechnology, and described the various reactor configurations currently being studied, as well as several commercialized systems. Recent findings with respect to the biochemistry of the microorganisms involved in anaerobiosis, their nutrient requirements, and toxicity were reviewed. Table 3-1 from his paper lists

TABLE 3-1. ORGANICS AMENABLE TO ANAEROBIC BIOTECHNOLOGY[a]

Acetaldehyde
Acetic anhydride
Acetone
Acrylic acid
Adipic acid
Aniline
1 amino 2 propanol
4 amino butyric acid
Benzoic acid
Butanol
Butyraldehyde
Butylene glycerol
Catechol
Cresol
Crotonaldehyde
Crotonic acid
Diacetone gulusonic acid
Dimethoxy benzoic acid
Ethanol
Ethyl acetate
Ethyl acrylate
Ferulic acid
Formaldehyde
Formic acid
Fumaric acid
Glutamic acid
Glutaric acid
Glycerol
Hexanoic acid
Hydroquinone
Isobutyric acid
Isopropanol
Lactic acid
Maleic acid
Methanol
Methyl acetate
Methyl acrylate
Methyl ethyl ketone
Methyl formate
Nitrobenzene
Pentaerythritol
Pentanol
Phenol
Phthalic acid
Propanal
Propanol
Isopropyl alcohol
Propionate
Propylene glycol
Protocatechuic acid
Resorcinol
Sec-butanol
Sec-butylamine
Sorbic acid
Syringaldehyde
Syringic acid
Succinic acid
Tert-butanol
Vanillic acid
Vinyl acetate
Corn
Potato
Sugar cane
Bagasse
Peat
Wood
Corn stover
Straw
Water hyacinths
Giant kelp
Animal wastes
Cheese whey
Pear wastes
Pectin wastes
Meat packing
Corn milling
Dairy
Brewery
Rum distillery wastes
Wine distillery wastes
Guar gum wastes
Water soluble polymers
Bean blanching
Pulp mill evaporate
Coking plant
H_2-CO pyrolysis
Wool scouring
Tannery wastes
Yeast
Wheat starch
Soy bean

[a] From Speece, 1983.

Industries - Wastes Amenable to Anaerobic Treatment

Chemical
Food Processing
Paper and Pulp
Sewage Sludge Treatment
Textiles
Pharmaceuticals

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organics, including specific industrial wastes, amenable to anaerobic biotechnology, and Table 3-2 lists various reactor configurations for anaerobic technology.

His summary of proprietary commercialized installations for industrial wastes is shown in Table 3-3; however, as pointed out in the paper, the anaerobic process itself is not patentable and there have been many other anaerobic installations designed, built and operated.

TABLE 3-2. REACTOR CONFIGURATIONS FOR ANAEROBIC BIOTECHNOLOGY[a]

Completely Mixed	(Conventional sewage plant digestors) one or two stage.
Anaerobic Contact Process	Completely mixed reactor with external settling, sludge recycle.
Upflow Anaerobic Sludge Blanket	Internal clarifier, gas separation with/without recycle of effluent.
Upflow Anaerobic Sludge Blanket	Utilizing external clarifier with/without recycle of effluent; sludge recycle.
Upflow Packed Bed	Various type media, usually submerged, with or without recirculation.
Downflow Packed Bed	Various media, usually submerged with or without recirculation.
Fluidized Bed	Recirculation of effluent to fluidize sand media; other type media possible.
Expanded Bed	Particle fluidization, dense media typically.
Combined Sludge Blanket Packed Bed	Upflow column with/without recycle.
Baffled Reactor	Series of upflow sludge blanket compartments, and internal clarifier with/without recycle.
Two Stage Leaching Bed - Leachate Filter	Batch feed solid waste, leachate, recycle to anaerobic filter.
Membrane - Anaerobic Reactor	Completely mixed reactor with membrane filtration for solids separation and return.

[a] From Speece, 1983.

TABLE 3-3. SUMMARY OF ANAEROBIC BIOTECHNOLOGY PROPRIETARY INSTALLATIONS[a]

Company	Process Name	Type of System	Number of Installations
AC - Biotechnical (formerly Sorigona)	ANAMET®	Contact mixed	US-3, Canada-1 World-27
Dorr-Oliver	ANITRON®	Fluidized bed	US-2
Bacardi	BACARDI®	Downflow filter	US-1
Badger (formerly Celanese)	CELROBIC®	Upflow filter	US-3
Biomechanics	BIOENERGY®	Contact - mixed	Europe-3
Ecolotrol	HY-FLO®	Fluidized bed	US-1
IRIS	-	Contact	Europe-7
Joseph Oat and CSM	BIOTHANE®	Upflow blanket	US-3, Europe-18

[a] After Speece, 1983.

The microbiology and biochemistry of the generation of methane from complex organics is rather complicated and in fact, all the details of the process and various interrelationships are not fully understood. There is, however, sufficient knowledge existing to rationally design and operate anaerobic treatment systems. The breakdown of complex organics initiates with the hydrolysis of fats, proteins and carbohydrates to sugars, amino acids and fatty acids. These substances are subsequently fermented to various intermediate products and short chain organic acids, alcohols, and hydrogen which are then converted to methane. There are different groups of microorganisms which, working independently and in symbiosis with other organisms, accomplish these steps, and in each group there are a variety of specific organisms. Substrate characteristics and environmental conditions established in the systems determine the predominance of species and their performance. Although complex, these factors are generally understood, some more than others. Application of a particular treatment system to a specific substrate (industrial waste), however, generally requires experimental evaluation to develop the design and operational paramaters for the industrial wastewater. Table 3-4 summarizes advantages and disadvantages of anaerobic treatment, compared to aerobic treatment which has been generally used for treatment of biodegradeable organic wastes.

TABLE 3-4. ADVANTAGES AND DISADVANTAGES OF ANAEROBIC VERSUS AEROBIC WASTE TREATMENT

Advantages

1. Lower energy requirements (no aeration).

2. Lower excess sludge production.

3. Lower nutrient requirements.

4. Greater ability to break down certain complex organics at high concentrations.

5. Production of useful end product, methane.

6. Depending upon reactor configuration and solids retention capable of significantly high loading rates, and smaller area requirements.

7. More economical potential, particularly for application to high strength wastes, and as a pretreatment component of a total treatment system.

Disadvantages

1. Slow growth requires longer start up and recovery from upsets.

2. Many wastes will require buffer additions.

3. Some wastes will require heating and maintenance of heat, or alternatively a much larger reacter, thus reducing economic advantages.

4. Off gas and effluent odors due to H_2S, sulfur compounds.

5. Effluent typically requires polishing (aerobic) treatment to meet discharge requirements.

6. Based on economic considerations, only strong wastes of COD > 2,000 mg/l are currently considered applicable to anaerobic treatment, however, research on dilute wastes indicates potentially favorable economics in this area also.

7. Limited full scale data base for design, particularly with the more recent innovations in reactor designs, and lack of full scale experience on specific waste streams. A significant pilot plant effort is required to develop design parameters.

ANAEROBIC CONTACT PROCESS

This process was initially developed as an anaerobic activated sludge system with a reactor and a separate clarifier and sludge return. Several years of research on milk waste in the late 1950s were reported,(5) in which 80 to 95 percent BOD removals, at loadings of 1.6-3.2 kg/m^3-d were achieved on a pilot plant basis. The system employed vacuum degasification prior to sedimentation to separate and concentrate the mixed liquor solids which were maintained at 5,000 to 15,000 mg/l. A full scale anaerobic contact plant to treat 5,300 m^3/day of meat packing wastewater was described in 1961.(6) The anaerobic digester provided 13 hours hydraulic detention time and contained a mixed liquor solids concentration of 7,000 to 12,000 mg/l. Vacuum degasification of the mixed liquor was followed by clarifiers, and settled sludge was returned to the reactor. Ninety percent BOD removal was achieved at 2.5 kg/m^3-d loadings.

The anaerobic contact process was investigated further with 30 liter bench scale reactors by Berg(7) to determine maximum loading rates with food processing wastes, which included pear waste, bean blanching wastes, potato waste and rum stillage. It was found that maximum loading and COD removal efficiencies depended markedly on the type of waste. At a COD removal efficiency of about 80 percent, the maximum volatile solids loading ranged from 1.6 kg/m^3-d for potato waste to 6.6 for bean blanching waste. The studies included identification of the need for nutrients, nitrogen, phosphorus, sulfur, and yeast extract in anaerobic treatment of these wastes.

Solids sedimentation on these type wastes was also investigated by Berg. He reported that various attempts to minimize settling problems, such as agitation, degasification, flocculating agents, and addition of inerts met with variable success. His findings indicated that there were variable initial settling rates, and it was difficult to interpret or predict results. Settling was affected by the reactor conditions; higher loadings reduced settling rates; flocculation had little beneficial effect; vacuum degassing effect on settlng was generally negligible; inert material addition had no noticable effect; and vibration increased initial settling rates, but slow agitation interfered in settling. The study suggested use of short distances such as inclined surfaces for settling, with a fill and draw cycle, to remove accumulated solids. Slow agitation could be used at solids concentrations up to two to three percent. In 1980, Berg further reported(8) on results of the anaerobic treatment studies summarizing the performance of anaerobic contact process on various food processing wastes. Removals of 65 to 90 percent of COD was achieved, and maximum COD loadings ranged from 2 to 10 kg/m^3-d, depending on waste characteristics.

The anaerobic contact process was commercialized in Europe as the Anamet® System by Sorigona.(9) The system included a mixed anaerobic contact reactor, degassification, clarification, sludge return, followed by an aerobic (activated sludge) system for complete treatment to meet effluent discharge requirements. This system(9) was developed for beet sugar wastewater in Sweden in approximately 1972. The results of pilot plant tests on wastes including dairy, vegetable, beet sugar, wheat starch, pulp and paper, citric acid, and rum distilling were summarized. Typical loadings to the anaerobic reactor ranged from 1 to 5 kg COD/m^3-d with COD removals of 50 to 80 percent, except for 60 percent COD removal from a pulp and paper waste. Organic loading on reactor solids ranged from 0.07 to 0.6 kg COD/kg MLSS-day. An estimated cost for a plant to treat 50 tons/day COD in a distillery waste was 2.0 to 2.3 million dollars, with annual operating costs of 250 to 300 thousand dollars per year (1981).

Eight full-scale Anamet® systems on beet sugar factory wastes and three other systems were reported on line(10) in 1981, with an additional seven systems expected to come on line in the subsequent two years, mostly on beet sugar and molasses wastes. The largest capacity plant of this type is in East Grand Forks, Minnesota (1980) which treats 38 tons/day BOD at 97.5 percent efficiency. Approximate cost reported for the Anamet® plants range from 1 to 5 million dollars for sizes to treat 10 to 100 ton COD/day, including both anaerobic and aerobic steps to provide overall BOD removal of 98 percent. The anaerobic portion was estimated at 75 percent of the above costs.

The performance of a full-scale Anamet® process system started up in the fall of 1982, was reported(11). The system treatment wheat starch waste containing an average of 13,600 kg COD per day. The anaerobic system operated at 35°C; the 5,700 m^3 anaerobic reactor was mechanically mixed; the mixed liquor was degassed, flocculated and settled in an inclined plate device. Sludge was returned to the anaerobic reactor, and the effluent was further treated by an activated sludge system. The BOD removal was 91 percent in the anaerobic stage, which was designed for a maximum loading of 3 kg/m^3-d. The system was estimated to produce an annual net energy gain of 37,400 x 10^6 BTU.

The upflow anaerobic sludge blanket process (UASB) developed in the Netherlands on food processing wastes was described by Lettinga(12) in 1979. Essentially this process is an upflow anaerobic sludge contact system, incorporating into the reactor a gas-solids separator. Mechanical mixing is not required and recirculation is at a minimum for good settling. The system design was based on the development of a good settling, anaerobic sludge. The process had been investigated since 1971 on a variety of food processing wastes in the laboratory (0.06 m^3), pilot (30 m^3), and full scale reactors (200 m^3). Maximum loading rates of 10 to 12 kg COD/m^3-d were obtained in the laboratory units, and somewhat lower loadings were obtained in the larger pilot and full scale units. Low initial loading, and a gradual buildup of loading over 8 to 12 weeks resulted in developing organic loadings of up to 0.8 kg COD/kg VSS-day.

Apparently calcium was found to be beneficial to sludge settleability in the upflow sludge blanket bed. The development of a granular, highly settleable sludge was noted in the lower regions of the reactor, forming a sludge bed with total solids of 100 to 150 g/l. Flocculating sludge predominated in the upper part of the bed. The tentative design surface load of 0.7 m/hr determined the depth to area ratio for a given plant and load. One inlet per 10 square meters of area was found adequate. Results from the pilot plant operated at 28 to 32°C, indicated over 90 percent COD removal for sugar wastes at 20 to 30 kg/m^3-d organic loading, and 4 m^3/m^2-d hydraulic loading. Similar removals at 14 to 16 kg/m^3-d were achieved on the full scale unit.

Acclimation of sludge in the upflow blanket process(13) in a pilot plant, to a sugar beet waste, achieved Sludge Volume Index values of 20 to 40 ml/gm for the flocculant sludge, and less than 20 ml/gm for the granular sludge, which gradually developed in the reactor. Loading rates of 30 to 40 kg COD/m^3-d at a COD to VSS ratio of 1.5 were achieved at a hydraulic loading of 8 m^3/m^2-d. It required about five weeks to develop a highly active biomass capable of being loaded at 7.5 kg/m^3-d. During the initial startup period a poorly settling sludge typically developed; it was, therefore, recommended(13) that the initial loading rate should be at the specific activity of the sludge, and gradually increased in small increments, after effluent volatile acids decreased to low levels. The doubling time of specific activity was about eight to nine days during the first few weeks, and the development of pelletization of the sludge occurred after six to seven weeks. At that point, loading could be increased fairly rapidly.

A full-scale UASB plant (800 m^3) treating beet sugar waste was described(14). The plant operated at 10 kg/m^3-d COD loading with 80 percent COD removal at a four hour hydraulic detention time and a temperature of 25 to 40°C. A hydraulic load of 1.5 m^3/m^2-h in the settler could be achieved without serious solids losses. With the beet sugar wastewater, approximately four percent of the dissolved COD was converted to bacterial sludge. It was determined that 1.5 to 2.0 kg COD/kg VSS-d could be converted to methane.

Lettinga(15) reviewed the UASB reactor concept in 1980. The gas solids separator can be quite simple, as shown in his original concept, as long as the surface load is below 0.7 m/hr, the inclined surface is 50°, and the flow in the opening between gas collectors is below about 2 m/hr. The main feature of the process is the development and retention of a highly settleable, active, granular type sludge. Granular sludge solids in the form of pellets were formed with a number of wastes, including potato processing, sugar beet, distillery and mixtures of volatile acids. It was not felt that an inert carrier, such as clay, was an important factor; however, presence of nutrients, flocculant conditions, calcium ions and a minimum of turbulent conditions were felt important. With low temperatures, or low strength wastes, provision for mixing, preferably by gas recirculation was suggested. The design COD loading rate at 35°C was indicated as five times that at 20°C. Based on fuel costs and the value of the methane produced, it was concluded that the cost of heating the waste and operating at the higher temperature would not be economically justified, based on a higher design COD loading and lower capital costs for the reactor.

The UASB process was further discussed by Lettinga (1983),(16) including factors involved in the formation of granular sludge with certain types of wastes. Complex wastes, high sulfides and high loadings were apparently detrimental to the formation of the granular sludge, which was reported easily formed with soluble carbohydrate type wastes (sugar, brewery, etc.) under proper conditions. It was suggested that the upflow sludge bed system be designed at 10 to 20 kg/m^3-d for soluble easily degradable wastes, and 9 to 10 kg/m^3-d for more complex wastes. It was also suggested that a two phase system or possibly a combined sludge bed and filter system be used for wastes which are complex, or do not form the granulated type sludge.

The UASB system is commercially available as Biothane® process in North America(17) and is based on the technology developed by a Dutch beet sugar firm. About 17 systems are reported in use world wide, treating mostly food industry (sugar beet, sugar, potato, starch, beer and alcohol) wastes. The largest system is in the United States and is a 4,700 m^3 reactor, designed for 14 kg/m^3-d and 80 percent COD removal, on brewery waste. Actual recent data reported(18) indicates that at 7 to 10 kg/m^3-d, COD removals of 75 to 85 percent are being achieved. At COD loadings of 8 to 14 kg/m^3-d, removal efficiencies generally in the range of 70 to 87 percent are being achieved by the Biothane® system on sugar, sugar beet, starch and alcohol wastes.(18) A system, recently put into operation, on a potato processing waste in Iowa,(19) was designed for 6 kg/m^3-d COD loading and 3,000 m^3 per day flow. Initial performance data indicates 80 percent COD removal at a loading of 1.5 kg/m^3-d.

The suspended growth contact process was discussed, and two full scale plants described.(20) Operating cost savings of \$0.10 to \$0.25 per pound BOD treated and capital cost savings of \$150 to \$400 per pound of BOD per day were reported for anaerobic treatment, compared to aerobic treatment. A plant designed to treat polymer wastes to achieve 85 percent COD removal was sized at 3.5 kg COD/m^3-d, four days detention, and an organic loading of 0.43 kg COD/kg MLVSS-day. The plant included the anaerobic reactor, a degassifier and a clarifier with sludge return. A plant designed for polysaccharide wastes was sized at 3 kg COD/m^3-d and COD to MLVSS at 0.3, to achieve 83 percent COD and 97 percent BOD removals. In this plant, the reactor effluent was cooled prior to the clarifier to enhance solids settling.

A relatively new concept, termed the anaerobic baffled reactor(21) has been studied. The system tested on a laboratory scale only, is an anaerobic sludge blanket process, using a series of verticle baffles, which result in a series of upflow and downflow compartments, which retain the biological mass. Loadings as high as 36 kg COD/m^3-d with 60 percent removal have been achieved and a model was developed to estimate reactor behavior over a range of waste concentrations and recycle ratios. A field scale system to evaluate the potential of this process is needed.

The Dorr-Oliver Membrane Anaerobic Reactor System (MARS) was described(22,23) in 1983. This system is a recent version of the anaerobic suspended growth contact system; however, unlike those with gravity solids separation, this system utilizes ultrafiltration membranes to separate solids in the flow from a mixed suspended growth anaerobic reactor. Biomass is returned to the reactor maintaining high solids concentrations, equivalent to fixed film systems. This system is reported to be especially suited to high strength, soluble wastes. Its selection over other anaerobic systems is based on economics, which are dependent upon the wastewater flow rate (less than about 2,000 m^3/d) and organic concentration (above 10 g/l). A pilot study on whey permeate achieved COD removals of 95 percent at volumetric BOD loadings up to 16 kg/m^3-d.

ANAEROBIC FILTER

The anaerobic filter for treatment of high strength soluble wastes was introduced by Young and McCarty(24) in the late 1960s. Their original concept involved a submerged rock media with a porosity of 42 percent, through which waste flowed upward. Initial laboratory studies at BOD loadings of 0.4 to 3.4 kg/m^3-d indicated a distinct loading--removal, relationship of 90 to 60 percent over this range, with a volatile acid waste and a synthetic protein-carbohydrate waste. Plummer et al.(25) conducted similar laboratory studies on a carbohydrate waste using raschig rings and saddles for media, which gave a porosity of 65 to 70 percent in the filter. These studies indicated good COD removals, greater than 80 percent at loadings up to 1.6 kg/m^3-d; however, a significant gradual drop in efficiency to less than 30 percent removal occurred at loadings up to 9.6 kg/m^3-d.

Dennis and Jennett(26) reported on their studies in 1974 using rock media laboratory anaerobic filters to treat high strength pharmaceutical waste. COD removals of over 90 percent were achieved at loadings of 0.2 to 3.5 kg COD/m^3-d.

In a paper presented in 1975, Mueller and Mancini(27) summarized 11 laboratory studies and one full scale study, on treatment of various types of wastes in anaerobic filters at COD loadings of up to about 10 kg/m^3-d. Their paper also presented a kinetic model of the anaerobic filter based on laboratory studies using 5/8 inch pall rings media. COD removal efficiencies of over 80 percent were obtained at loadings up to 6.4 kg/m^3-d, and 46 to 69 percent removals were obtained at loading rates of 27 kg/m^3-d for an easily degraded synthetic protein carbohydrate waste. Based on measured void volume reduction due to biological growth and retention as a function of COD removal, an extrapolation of data indicated that the filter would eventually clog with solids at a loading of about 18 kg/m^3-d.

Hudson et al.,(28) investigated the treatment of shellfish processing wastes using rock and oyster shell media anaerobic filters. Loadings of

0.15 to 0.34 kg COD/m^3-d were studied and removals of approximately 80 percent were obtained.

Sachs(29) reported on the laboratory rock anaerobic filter treatment of pharmaceutical wastes in which COD removals of 70 to 80 percent were achieved at a loading of 1.7 kg COD/m^3-d. However, increased waste concentration caused a decrease in efficiency to 18 percent removal, possibly due to a short acclimation period or the strong, possibly toxic, waste.

Donovan(30) presented summarized results from 12 months of pilot plant studies using a full size pall ring media with a porosity of 95 percent in upflow anaerobic filters treating a sewage plant sludge heat treatment liquor. A COD loading of about 9 kg/m^3-d was achieved after four and a half months of operation with COD removals of 50 to 60 percent; and BOD removals of 78 percent. Concurrent laboratory unit studies with 5/8 inch pall ring media gave comparable removals at two to three times the loadings on the full scale media. A suggested design of a full scale system at a loading of 7.5 kg/m^3-d was presented, and compared to aerobic treatment of the waste. Significant capital and operating cost advantages of the anaerobic filter were determined.

The first full-scale anaerobic filter was operated on a wheat starch gluten wastewater in 1971 in Spokane, Washington. Taylor(31) reported on 15 months of monitoring the rock filled filter used to pretreat the waste prior to discharge to the city sewers. Three wood stave tanks, operated in parallel, were 30 feet in diameter and 20 feet high. The COD loading was 3.8 kg/m^3-d and an average removal of 64 percent was obtained.

Witt et al.,(32) presented results of the Celenese, Vernon Texas full scale anaerobic filter started up in mid-1977. The treatment plant was built to treat wastes from processing quar beans prior to discharge to the city system. Pilot studies indicated COD removals of 64 to 70 percent at loadings as high as 18 kg/m^3-d. The 1,020 m^3 full scale filter was operated at about 7.5 kg COD/m^3-d and achieved an average of 50 percent COD removal. Also reported was the performance of laboratory pilot units on several chemical waste effluents which indicated COD removals of generally over 85 percent at loadings in the range of 4 to 14 kg/m^3-d. Effluent recycle was incorporated to mitigate toxic concentrations of certain organics and to provide buffering capacity, which minimized plug flow characteristics in the filter. Based on the successful and economical results the plant was to be more than doubled in capacity.

Ragan(33) subsequently reported on Celanese's commitments to install anaerobic filters at their Bishop and Pampa plants prior to aerobic treatment systems. The waste flows were approximately 3,800 m^3/day. The Bishop waste contained about 35,000 and the Pampa plant 53,000 kg COD. The Bishop wastewater is from the manufacturing of a variety of oxygenated organic chemicals, including methanol, formaldehyde, butanol, polyols, and polyacetal copolymer resins. At Pampa, wastes are from manufacturing of acetic anhydride, methylethylketone, ethylacetate and methylformate. Significant energy savings and credit for methane were reported to be valued at up to $730,000 per year, based on treating 23,000 kg COD per day.

Sheridan(2) further reported on the three full scale plants. After three years of operation at the Vernon plant, solids plugging occurred and required the development of a proprietary biological solids control system. Effluent recycle capabilty was included in the new designs to minimize the effect of toxic concentrations in the waste and to provide buffering of the wastes. The Bishop and Pampa systems came on line in 1981 with the biomass control system to mitigate problems resulting from reactor channelling and plugging. The reactors were sized for 5,700 m^3 and designed for loadings of 9 and 11 kg COD/m^3-d and 80 percent and 90 percent COD removal, respectively.

Szendrey(34,35) described Bacardi's® design of an anaerobic filter for treating rum distilling wastewater. The filter utilizes BF Goodrich plastic Vinyl-Core® media (a series of sinuous tubes). The filter is submerged, and flow is from top to bottom with liquid recirculated from the bottom to the top by external pumps. The filter containing 9,600 m^3 of media 9.5 m deep, was designed for a flow of about 1,050 m^3/day containing 41,000 kg BOD, 97,000 kg COD. The COD loading was about 10 kg/m^3-day. Recent (1983) data indicated BOD removals of 69 percent at a BOD loading of 5.3 kg/m^3-d. Capital and operating cost data were provided. The total capital cost was 8.3 million dollars and 1982 operating and maintenance costs were $275,000 or $0.0183 per pound of BOD removed. A significant reduction to $0.01 per pound of BOD removed was predicted for 1983. The gas produced is used in the distillery and is expected to be the equivalent of 1,400,000 gallons of fuel oil in 1983.

FLUIDIZED BED--EXPANDED BED REACTOR

Development of fluidized bed reactors for anaerobic treatment was a result of the extension of the use of packed beds for denitrification of nitrified sewage effluents. Jeris(36) described the initial development of a fluidized bed reactor using carbon as a medium for denitrification in 1974, to eliminate clogging problems in packed bed reactors. The initial tests indicated a capacity of the process to handle high hydraulic and nitrogen loadings at low hydraulic detention times. The process developed, named Hy-Flo , was further described(37) in 1977. Pilot plant studies, (1973 to 1975) both aerobic and anaerobic (denitrification), were conducted at the Nassau County Bay Park Sewage Treatment Plant, New York, using sand as the media, during which the technology was further developed. It was concluded that the technology should be significantly less expensive than conventional treatment. Removal of 93 percent BOD with a 16 minute detention time and 99 percent ammonia nitrification with an 11 minute detention time were reported in two aerobic fluidized bed systems in series. An anoxic fluidized bed system, in series resulted in 99 percent nitrate removal in 6.5 minutes.

Bell(38) reported on a pilot scale study conducted in Jacksonville, Florida, in 1978 with a fluidized bed anaerobic reactor, treating decant liquors from thermal conditioning of a waste biological sludge. Removal of 70 percent COD at a loading of 7.6 kg/m^3-day and 49 percent removal at a loading up to 26 kg/m^3-d, were reported. The unit was operated at 31 to

38°C and a pH of 7.35. The flux rate in the bed was 27 m/hr to fluidize the sand media used.

The fluidized bed treatment process was licensed to Dorr-Oliver in 1976 and named the Anitron® (anaerobic) and Oxitron (aerobic) systems. Interim results of Anitron® pilot plant studies on a whey waste and a soy processing wastewater were reported.(39) Removals of 63 and 68 percent COD at loadings of about 10 kg/m^3-d were obtained at 30 to 35°C on the whey waste using 0.7 and 0.5 mm sand media, respectively. The larger sand required about double the recycle flow to maintain 30 to 50 percent bed fluidization. At a loading of 5 to 7 kg/m^3-d the 0.5 mm sand bed achieved 82 percent COD removal with an influent waste concentration of 27,350 mg/l COD. Other studies on carbohydrate wastes were reported(39) to have achieved 80 percent COD removals at loadings of 16 kg/m^3-d. The pilot study on soy bean waste was conducted at 35°C and pH 6.7 to 7.0. BOD removals of 83 to 89 percent were reported at total BOD loadings of 7.8 and 9.3 kg/m^3-d. A full scale system was designed at a BOD loading of 9.3 kg/m^3-d and was scheduled to startup in late 1981. The full-scale Anitron® system for the soy bean waste was further described.(22,23) The system consisted of four reactors each 6.1 m in diameter with a 10.4 m bed height. Hydraulic rate was 24 to 39 m/h, operating temperature 35°C and pH 6.8 to 7.2. Actual startup was delayed until spring of 1982, due to construction delays.

The fluidized bed system has also been studied as a two phase anaerobic system,(23) which, depending upon waste characteristics, may be both technically and economically beneficial. A summary of wastes studied (1983) with the fluidized bed included soy bean, dairy whey, wheat starch, corn starch, paper mill whitewater, evaporator condensate, Kraft mill decanter, dairy industry cheese processing, brewery wastes, and sludge heat treatment liquor. Costs of the Anitron® system depend upon the COD loading selected for design. Current installed costs estimated for the system range from approximately $250,000 for a very small plant, COD 1,000 kg/day; to $600,000 for a 10,000 kg COD/day load; and $3,000,000 for a 180,000 kg COD/day wastewater load.

Jeris(40) reported on a number of pilot plant studies using the anaerobic fluidized bed reactor. In one study on a waste containing soluble and colloidal corn starch and protein, it was found that BOD removals ranged from 93 to 87 percent at loadings from 3.5 to 24 kg/m^3-day. On a whey waste of 50 g/1 COD, removals of 65 to 84 percent were achieved at loadings of 37 to 13 kg/m^3-d. On the whey waste, COD removals of 80 percent were achieved at 10 kg/m^3-d in a single unit and 93 percent at an overall loading of 10 kg/m^3-d with two units in series. Data from the whey waste studies indicated a 10 percent reduction in removal efficiency at 24°C compared to 35°C. Other wastes studied included food, chemical, soft drink, bakery, and heat treatment liquor, ranging in COD from 5,000 to 11,000 mg/1. Removals of 68 to 93 percent at loadings of 27 to 3 kg COD/m^3-d and detention times of 0.3 to 2.8 days were reported. The data illustrated that removal efficiency for these wastes was almost constant at loadings up to 16 kg/m^3-d, and for the whey waste efficiencies remained high at loadings up to 36 kg/m^3-d. About 0.4 liters of methane was produced per gram of COD removed. A comparison of energy requirements with aerobic treatment indicated a significant advantage of the anaerobic process. Solids production estimates based on COD removal for these wastes ranged from 0.024 to 0.083 kg/kg COD removed. Further optimization of the fluidized bed system was felt necessary. In particular a determination of the optimum media size and density to minimize recirculation requirements yet permit optimum biological solids control, needed to be made. Also seen as areas requiring additional study with respect to media selection were temperature, waste characteristcs, and density and film thickness of biomass developed. Operational control and maintenance of the process were also seen as areas requiring further optimization.

A pilot plant study for an anaerobic fluidized bed pretreatment of bakery wastewater was conducted.(41) The COD of the waste was about 8,800 mg/1 and removals of 80 percent at loadings of 10 to 14 kg/m^3-d were achieved. Based on waste variations, an average design loading of 8.8 kg/m^3-d was selected to treat the 270 m^3/day flow. Economic analysis demonstrated that the project would be economically feasible, providing about a 20 percent return on the owners capital, compared to paying relatively low sewer system surcharges.

The anaerobic attached film expanded bed (AAFEB) process, which is essentially a fluidized bed modification (expansion average of 10 to 20 percent) has been studied on a laboratory scale for a number of years.(42,43) The studies showed potential for treating relatively dilute wastes, glucose at 200 to 600 mg/l COD, and domestic sewage primary effluent at low temperatures, at organic loading rates in the range of 1 to 8 kg/m^3-d. Whey waste(44) treatment with the AAFEB at various concentrations, 5 to 20 g/l and loadings, 8 to 60 kg/m^3-d was studied. Over 80 percent COD removals were achieved at loadings up to 20 kg/m^3-d, with gradual decreases in removal efficiency with increased loadings up to 60 kg/m^3-day.

COMPARISONS OF VARIOUS ANAEROBIC TREATMENT METHODS

The upflow filter suspended growth contact process with external clarification and sludge return, and the upflow sludge blanket process with internal sludge separation were compared,(45) using relatively small laboratory scale reactors for treating glucose, or saccarin and sodium acetate substrates. The units were compared at optimum reactor loadings, defined as the highest possible loading with COD removals of 90 percent and without fatty acids in the effluent (less than 50 mg/l). The loadings found were quite low (0.5 to 3.5 kg TOC/m^3-d); however, the findings were of interest. The study concluded that: (a) mixing seemed to be of no benefit in the suspended growth or sludge blanket process, and (b) the upflow sludge blanket reactor gave the best results. Ninety percent removals, at a TOC loading of 2 kg TOC/m^3-d with a carbohydrate feed, and a loading of 12 kg TOC/m^3-d with a volatile acid substrate, were reported with the sludge blanket process. Separation of the acid forming and methane fermentation steps would produce better results since significantly higher organic loading rates could be achieved. Washout of sludge (methane formers) was experienced with the upflow filter unit and the stirred upflow sludge blanket reactor, however, washout was not observed in the upflow sludge blanket reactor without stirring.

A comparison of upflow and downflow anaerobic fixed film reactors was conducted,(46) using small laboratory reactors of varying diameters from 1.0 to 7.5 cm, and from 0.087 liters to 4.86 liters volume, and a bean blanching waste, COD 10,500 mg/1. A maximum loading rate of 15 kg volatile solids/m^3-day and COD removals of 80 to 93 percent were achieved. It was concluded that fixed film reactors could effectively remove COD anaerobically at significantly high rates. Slow initial development of the film was seen as a disadvantage. It was found that in the downflow mode, the reactor operated as a fixed film reactor only, while in the upflow mode, solids concentrations in the liquid acted as a partially fluidized bed, thus increasing potential loading rates and efficiency. The potential disadvantage of plugging was mentioned, but had not been experienced in these studies.

A comparison of anaerobic treatment efficiency with fixed film, suspended growth contact, and mixed digesters was made(47) on small scale reactors using a soluble bean blanching waste and a simulated sewage sludge. Loadings were increased stepwise to the reactors when volatile acids concentration of 200 to 400 mg/1 were achieved, until maximum loadings were achieved. The results are summarized in Table 3-5. Based on the results, it was noted that the lower minimum detention time for the fixed film reactor indicate this reactor's ability to retain more active biomass than the other two. This was particularly true for the more soluble bean blanching waste. The COD removal efficiency depended on waste and reactor. It was noted that the fixed film reactor was more stable at the maximum COD loading than the contact digesters. The fixed film reactor did not degrade cellulose in the sludge substrate as well as the anaerobic contact digester; however, there was intense mixing in the fixed film unit once gas production increased. This gas mixing apparently explained why the fixed film reactor could use dilute and concentrated wastes equally well. As noted, the soluble waste strength fed to the contact digester was increased to achieve the minimum hydraulic retention and maximum organic loading. A maximum loading on an 0.7 liter fixed film unit of 20 kg/m^3-d was achieved, independent of waste strength which was varied from 5,000 to 20,000 mg/1 COD. The higher loadings possible on this unit were attributed to a greater surface area to volume ratio than in the 35 liter unit. The completely mixed reactor was limited by minimum hydraulic time. The potential advantage of the fixed film reactor over the suspended growth contact process included elimination of mixing, sludge settling and return, as well as better stability at high loading rates.

TABLE 3-5. PILOT PLANT DATA

	Bean Blanching Waste 9,500 mg/l COD			Simulated Sewage Sludge 55,000 mg/l COD		
	Fixed Film	Contact Digester[a]	Mixed Digester	Fixed Film	Contact Digester	Mixed Digester
Reactor Volume (liters)	35	30	2	35	30	30
Minimum Hydraulic Detention, days	1	3	8.5	4.5	5.5	8.5
Maximum COD Loading kg/m^3-d	10	7	1.2	12	10	6.5
Percent COD Removal	86	80	75	70	74	65

[a] Feed at 20,000 mg/l COD.

From Reference.(47)

Performance of fixed film and upflow sludge bed reactors on different wastes was compared,(48) based on the results from various studies with small laboratory scale reactors of 1 to 35 liters volume. Data indicated the fixed film reactor could treat wastes of 4 to 140 g/l COD at detention times as low as 0.5 days. Attaining a high loading rate, 14 to 18 kg/m^3-d, was dependent on type and strength of the waste. The units could operate at temperatures as low as 10°C, although the maximum loading rate decreased with temperature. The units could be restarted quickly (one to two days) after long periods of no waste feed, and recirculation of effluent (up to 50 times influent flow) did not noticeably affect performance. The sludge bed reactor typically handled slightly higher COD loading rates of 12 to 30

kg/m^3-d, and had slightly higher COD removal efficiencies than the fixed film reactor; however the sludge bed reactor was more difficult to startup. At low waste strength, 3 g/l COD bean blanching waste, and a loading rate of 12 kg COD/m^3-d, the hydraulic residence time became too short and the COD removal efficiency dropped to 50 percent in the sludge bed reactor. Recirculation ratios from 1 to 50 did not affect the sludge bed reactor performance; however, sufficient recirculation was required for mixing. It was suggested that an external settler, while not required for all types of wastes, would increase overall reliability and flexibility of the upflow sludge bed process, and could simplify the reactor construction. The sludge bed reactors were found to be more sensitive to temperature changes and waste composition than the fixed film reactor.

Ten months of startup and one month of a steady state period results from anaerobic pilot studies were reported by Hall.(49) The study evaluated the performance of four types of anaerobic reactors treating a thermal sludge conditioning supernatent, which had a COD of 11,000 mg/l. The pilot plants included: (a) a downflow stationary fixed film system, containing 280, 2.5 cm tubes 1.8 meters deep; (b) a USAB bed with an internal gas liquid separator; (c) an upflow anaerobic filter, with 9 cm pall ring media; and (d) a skid mounted fluidized bed with 0.7 mm sand media expanded 22 percent. The reactor volumes of the first three pilot plants were one cubic meter and the fourth was 0.042 cubic meters. The pilot units were operated at 35°C and a pH of 6.8 to 7.2. Seeding was with municipal digester sludge, and loadings to the unit were increased when volatile acids decreased to less than 500 to 1,000 mg/l. Caustic was used to maintain pH during high volatile acid periods. In the fluidized bed it was necessary to increase volatile acids to 2,000 mg/l to produce a response in COD removal capacity. There was considerable difficulty in starting up the UASB system, due to sludge washout, and reseeding was required. Various corrective actions were attempted, including the elimination of recycle and improvements of gas liquid separation which, however, were not adequate. It became necessary to clarify the reactor effluent externally, and return solids. In this mode, a loading of 7 to 8 kg COD/m^3-d could be maintained. After one year, the biomass was still very susceptible to washout when loading was increased. No granular sludge was observed in the unit. After 10 months, loadings of 30 kg/m^3-d were attained in the three fixed film systems. Results during a 30 day steady state performance at 35°C, 12,400 mg/l influent COD and pH 6.9 to 7, were summarized as follows:

	Upflow Filter	Downflow Fixed Film	Sludge Blanket	Fluidized Bed
Detention Time, Hr	14.3	15.0	49.0	13.3
COD Loading kg/m^3-d	20.6	19.1	5.9	21.7
Percent COD Removal	67	58	71	50
Gas Yield $m^3/kg\ COD_R$	0.37	0.35	0.4	0.31
Percent CH_4 in Gas	65	60	65	68

Note: Approximately 20 percent of the COD was non-biodegradable.

The lower removal in the fluidized bed was attributed to lower solids in the unit as a result of shear forces, due to the high recycle rate of 65 m/hr, required with the 0.7 mm sand media. A subsequent study(50) using smaller media (0.5 mm), resulted in improved performance on a brewery wastewater. It was also mentioned that the sludge blanket unit did develop the granular sludge when treating brewery wastewater.

Hall further reported on the pilot plant studies.(50) Results on brewery waste at similar loadings, of 20 kg/m^3-d, showed COD removals of 90 percent in the filter; 76 percent in the downflow fixed film; 77 percent in the upflow sludge bed, and 98 percent in the fluidized bed (smaller media). COD loadings, up to 20 kg/m^3-d, had a very significant effect on removal efficiency in the downflow fixed film unit; a moderate effect in the filter, and essentially no effect in the sludge blanket and fuidized bed units. Effluent solids from the fluidized bed were the lowest at 150 mg/l and averaged about 300 mg/l from the upflow blanket and over 500 mg/l from the filter and fixed film units. Solids yield was similar on the units, 0.02 to 0.1 kg/kg COD_R and methane averaged 0.21 to 0.32 $m^3/kg\ COD_R$. Tracer studies showed that all the systems were essentially well mixed. It was concluded that performance of the various systems is closely related to the specific wastewater characteristics.

Berg(51) in a comparison of advanced anaerobic reactors and their design, discussed applications and limitations of the various systems. He suggested COD loading design ranges for food processing wastes of up to 6 kg/m^3-d for the contact process; 10 kg/m^3-d for the anaerobic filter; 20 kg/m^3-d for the fluidized or expanded bed; 15 kg/m^3-d for the downflow fixed film reactor, and 30 kg/m^3-d for the upflow anaerobic sludge bed. Also discussed were staged reactors to separate the acid forming phase and the methanogenic phase which were felt to be potentially useful under certain circumstances. Because of cost and complexity, however, it was indicated that staged reactors were not likely to find widespread application.

TREATABILITY OF SULFITE LIQUOR CONDENSATE

Anaerobic treatability of an acid wastewater (condensate from evaporation of spent sulfite liquor) was determined in laboratory reactors.(52) The condensate containing acetic acid, furfural, and sulfur compounds was fed to batch and continuously mixed laboratory units operated at 35 and 60°C. Mineral nutrients considered essential for growth of the anaerobic bacteria were added to the waste. After gradual acclimation over 12 to 14 weeks, more than 90 percent of the TOC in the wastewater was converted to biogas. At retention times shorter than 10 to 12 days, washout of the bacteria occurred; however, with external sedimentation and recycle, hydraulic detention time in the reactor could be shortened to 3 days. A 150 liter upflow sludge blanket unit was successfully operated. A batch study using an acclimated sludge showed initial inhibition to a waste feed containing 0.7 g/l of furfural. The furfural was converted to acetic acid after about an 8 day lag period, and the gas production increased rapidly about 40 days after feeding.

A year and a half laboratory study evaluated the use of anaerobic filters to treat sulfite evaporator condensate(53) from a calcium bisulfite mill. The laboratory units were about 19 liters in volume and contained plastic media with a porosity of 90 percent. At organic loadings of up to 16 kg/m^3-d, 79 to 90 percent COD reduction was achieved. Excess solids production was determined to be 0.09 kg/kg COD removed. About 0.4 m^3 gas/kg COD containing 76 percent methane was produced. Toxicity from sulfur compounds, furfural or trace organics was not a problem. Consistent results were only obtained after adding a suite of trace nutrients and sufficient alkalinity (caustic and bicarbonate were used) to neutralize all of the acid in the feed to pH 6.8. This resulted in an effluent pH in the range of 7.2 to 7.6. A test in which waste feed strength was varied indicated that variations typical in a sulfite mill would not upset the system as long as pH and alkalinity addition were maintained. Pulsed loadings of spent sulfite liquor were also fed to the units to simulate washdowns or process upsets in the evaporator. The tests indicated, within the range of loads tested, that the spent sulfite liquor mixture did not result in any deterioration in the performance of the filter. Preliminary measurements indicated that about 50 percent of total sulfur was removed. Short term studies indicated that sulfide odor in the effluent could be removed by aeration.

The toxicity of sulfite evaporator condensate to methanogens was studied using batch bioassays.(54) Study results indicated that significantly higher concentrations than were present in sulfite liquor, of furfural, guaiacol, p-cymene, and eugenol were required to cause inhibition to gas production.

A laboratory study on treatability of evaporator condensate was conducted on an ammonia based sulfite liquor evaporator condensate similar to that at the Procter and Gamble, Mehoopany plant.(55) The condensate was found to be highly degradable both aerobically and anaerobically. An acclimation period of about 20 days was used to introduce sulfite liquor to a laboratory anaerobic filter using stone media. After about 40 days, 85 to 90 percent COD removals were achieved at a detention of 1 to 1.3 days, and loadings of 12.7 to 16.5 kg COD/m^3-d. An anaerobic toxicity assay indicated that the waste at 20 percent by volume in the reactor required 20 days for acclimation, and at 40 percent was inhibitory to methanogenesis during the 30 day test. Recycling of effluent was used to dilute the influent to the filter.

SECTION 4

SCREENING STUDIES

During the pilot plant construction period, samples of the wastewater were collected and analyzed. Laboratory scale anaerobic treatability tests were conducted on these wastewater samples to gain information on the treatability of the waste. Objectives of the screening studies were to determine if there were any potential problems in treating the waste, to develop startup/acclimation procedures, to obtain preliminary loading parameters, and to gain experience in analyzing waste samples.

WASTE CHARACTERIZATION

Preliminary data on foul condensate characteristics received from Procter and Gamble are shown in Table 4-1.

TABLE 4-1. PRELIMINARY RAW FOUL CONDENSATE ANALYSIS[a] 1982

	Evaporator 8-CPT	Evaporator 8-CPT	Evaporator 8-CPT	Evaporator 7-CPT	Evaporator 7-CPT	Low Feed Rate	Low Feed Rate
Sample Date	7-20-82	8-17-82	8-19-82	7-27-82	8-10-82	8-24-82	8-26-82
Color	300	500	688	433	375	292	500
Conductivity	2.8	7.2	7.0	11.4	11.3	-	6.0
pH	2.09	2.38	2.31	2.23	2.72	2.66	2.53
BOD (mg/1)	10,500	9,280	9,920	11,000	9,450	12,300	10,500
COD (mg/1)	20,000	20,000	50,500	17,000	17,000	19,600	16,400
Furfural (%)	0.15	.16	.16	.18	.13	.15	.17
Acetic Acid (%)	-	.94	.99	-	.83	.92	.93
NH_3-N (mg/1)	56	37	37	82	110	51	57
Total N (mg/1)	73	22	34	60	124	56	52
Sulfide (mg/1) as S	-	115	-	-	-	102	-
Sulfite (mg/1) as SO_3	-	452	-	-	-	221	-
Sulfate (mg/1) as SO_4	-	66	-	-	-	72	-
Total Sulfur (mg/1)	-	382	-	-	-	214	-

[a] Received from Procter and Gamble.

Conditions

Evaporator 8-CPT - All eight compartments in evaporator operating.

Evaporator 7-CPT - Seven compartments in evaporator operating.

Low Feed Rate - Sulfite liquor feed rate to evaporator below normal (actual rate not recorded).

The data indicate a fairly consistent, low pH waste, containing acetic acid and furfural, a COD of about 20,000 mg/l, and a BOD of about 10,000 mg/l. The waste contained ammonia nitrogen and several forms of sulfur. The initial sample collected for the screening treatability studies was analyzed and the results are shown in Table 4-2.

TABLE 4-2. FOUL CONDENSATE CHARACTERIZATION (SEPTEMBER 1, 1982)

Analysis	Concentration (mg/l)
pH (units)	2.0
TDS	98
BOD	10,800
COD	20,000
TOC	6,420
Sulfides as S	<.1
SO_3 as SO_3	35
SO_4 as SO_4	68
Total Sulfur as S	85
Mercaptans	<.1
Acidity as Ca CO_3	9,500
TKN as N	41
NH_3 as N	38.6
O-Phosphate as P	0.13
Furfural	1,170
Methanol	1,290
Ethanol	<1
Acetic Acid	12,800
Suspended Solids	<1
Na	2.0
K	<0.4
Ca	5.7
Mg	0.66
Ni	<.05
Zn	1.02
Co	0.06
Se	<0.01
Cr	<0.05
Cu	2.48
Fe	0.21
As	<0.10

The waste sample was low in nonvolatile dissolved solids, including metals, phosphorus, and nitrogen, which are required nutrients for anaerobic biological treatment.

Neutralization

Figure 4-1 presents pH titration curves for a waste sample using caustic and calcium hydroxide. Total acidity of the sample was about 10,000 mg/l as $CaCO_3$.

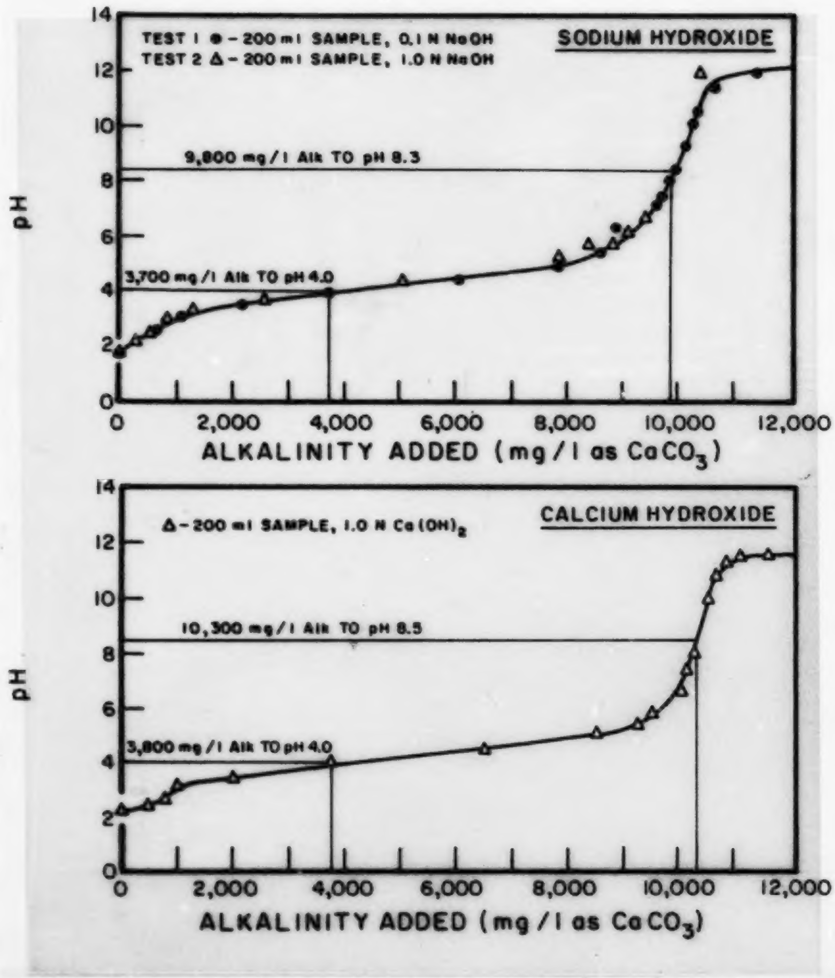


Figure 4-1. Condensate wastewater pH titration curves.

Acidity, below pH 4.0, was about 3800 mg/l. Since the samples contained primarily acetic acid, which would depress pH to 2.8 to 3, the acidity below 3.0 could be attributed to minerals, i.e., sulfur compounds. This mineral acidity due to the sulfur compounds was in the range of 500 to 1000 mg/l. The titration curves are essentially identical to a titration curve for acetic acid, except for the tail below pH 2.8.

An anaerobic biological treatment system pH range of 6.5 to 7.5; thus neutralization of the waste would be required. As acetic acid is degraded and CO_2 gas emitted, the bicarbonate alkalinity in the waste will increase; thus all of the acetic acid in the raw waste does not need to be neutralized. The extent of neutralization required is related to neutralizing the mineral acidity, the actual volatile acid concentration in the anaerobic reactor, and the carbon dioxide dissolved in the reactor liquid.(56) Based on maintaining reactor volatile acids in the range of 1000 to 4000 mg/l, an estimated off-gas concentration of CO_2 of about 30 to 35 percent, a mineral acidity of 500 to 1000 mg/l, and reactor pH of 6.8 to 7.2, a neutralization requirement can be determined. The range of alkalinity additions required to maintain a reactor pH of 7.0, would be approximately:

	Alkalinity Requirements (mg/l as $CaCO_3$)
Mineral Acidity (500 to 1000 mg/l)	500 - 1000
Volatile Acids (1000 to 4000 mg/l)	800 - 3300
CO_2 (30 to 35 percent in off-gas)	1800 - 2500
Totals	3100 - 6800

Lime (calcium hydroxide) typically is used to raise pH in municipal sludge digesters, and is significantly less costly than caustic (sodium hydroxide). Studies have been conducted which indicate inhibition to the biological process due to excess concentrations of sodium and calcium ions, may occur in anaerobic digestion.(57) It was decided to initially neutralize with both lime and caustic; since if only one cation were used, the inhibitory concentrations would be approached.

Nutrient Addition

The waste, an evaporator condensate, would be expected to contain only volatile compounds carried over, and as indicated by the wastewater analyses, would be nutrient deficient. Major nutrients for biological treatment include nitrogen and phosphorus. In addition, other trace elements were identified or indicated as required for anaerobic biological treatment(52) of evaporator condensate. Typically, in most waste treatment systems, trace elements are usually present in the carrier water or waste. With the evaporator condensate, it was possible that there would be significant deficiencies. Required nutrients are listed in Table 4-3. Chemical compound sources and the concentration of each element in the foul condensate wastewater, to ensure biological treatment would not be limited by nutrient defficiency, are also listed.

TABLE 4-3. NUTRIENT ADDITIONS FOR FOUL CONDENSATE BIOLOGICAL TREATMENT

Chemical Compound	Nutrient Element	Concentration of Element in Waste After addition (mg/l)
Ammonium Chloride	N	50 - 100
Potassium Phosphate	P	30.0
Nickel Chloride	Ni	0.25
Ferrous Chloride	Fe	4.0
Cobalt Chloride	Co	0.1
Selenious Acid	Se	0.005
Sodium Tungstate	W	0.02
Ammonium Molybdate	Mo	0.02
Zinc Chloride	Zn	0.02
Vanadium Chloride	V	0.02
Manganese Chloride	Mn	0.4
Lime[a]	Ca	20.0
Boric Acid	B	0.01
Thiamine HCl	-	0.1
Pantothenic Acid	-	0.1

[a] Commercial grade-- also contained 1 percent magnesium.

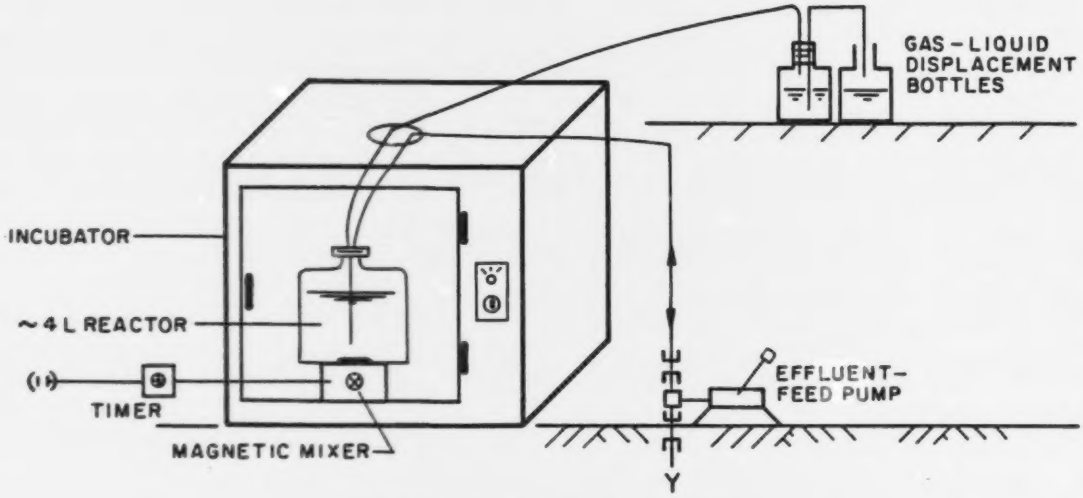
During the screening studies, nitrogen and phosphorus were added to the waste, but trace nutrients were not. The initial sludge seed obtained from an active digester was assumed to contain adequate nutrient concentrations.

DESCRIPTION OF LABORATORY APPARATUS AND ANALYSES PROGRAM

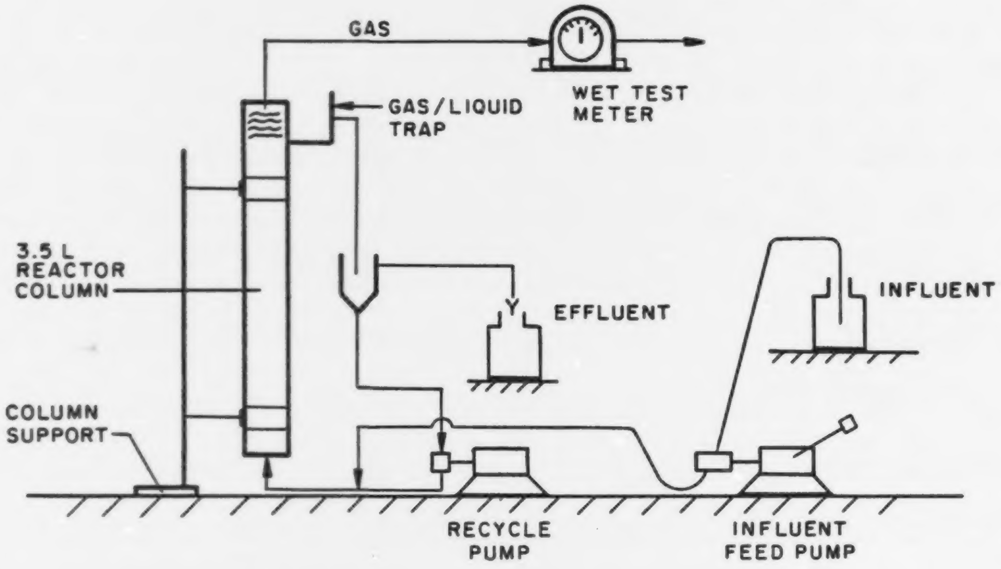
Three 4 liter bottles (reactors A, B and C) were set up in incubators which maintained temperatures at 31 to 36°C. The contents of the reactors were mixed by timer controlled magnetic mixers. Gas emitted from each reactor was collected under water and measured by liquid displacement. A small laboratory pump was used to remove reactor contents and add waste feed. The units were fed only once a day. The frequency of feeding was based on volatile acid concentrations. Figure 4-2 illustrates the laboratory setup.

Two 3 liter plastic column reactors, (D and E), were set up as continuous anaerobic units. The columns were 120 cm high and 6.25 cm in diameter. Temperature was maintained at 32 to 35°C by a heating tape around the columns controlled by reactor temperature measurements. One column contained 5/8 inch pall rings to simulate a fixed media reactor, the other was operated as an upflow sludge blanket unit. Effluent from each reactor was collected in a small bottle and recirculated to the reactor bottom by a laboratory pump. Influent was added to the recirculated effluent by a timer controlled feed pump. Gas was collected at the top of each reactor column and measured using a wet test meter. The continuous laboratory unit is also illustrated on Figure 4-2.

The basic monitoring and analytical schedule followed with the laboratory units is shown in Table 4-4. This schedule was followed as necessary, and was modified during the study period. Effluent COD measured on filtered samples, volatile acids, and pH were the key parameters tracked in the screening study, along with gas measurements. Operating and analytical data are included in tables in the Appendix, Volume 2.


GAS-LIQUID DISPLACEMENT BOTTLES
INCUBATOR
~4 L REACTOR
TIMER
MAGNETIC MIXER
EFFLUENT-FEED PUMP

BATCH ANAEROBIC REACTOR


GAS
WET TEST METER
GAS/LIQUID TRAP
3.5 L REACTOR COLUMN
EFFLUENT
INFLUENT
COLUMN SUPPORT
RECYCLE PUMP
INFLUENT FEED PUMP

CONTINUOUS ANAEROBIC REACTOR

Figure 4-2. Schematic laboratory screening study reactors.

TABLE 4-4. MONITORING SCHEDULE LABORATORY SCREENING TESTS

Analysis	
gas production	5/week
gas analyses	1/week
Influent Feed	
COD	1/week
pH, acidity	1/week
volatile acids	1/week
flow and volume	daily
Effluent	
COD$_F$	3/week
flow and volume	daily
pH	3/week
alkalinity	3/week
volatile acids	3/week
temperature	daily
suspended solids, volatile suspended solids	Intermittently

SCREENING STUDY RESULTS

Batch Reactors

The units were set up and the temperature controls, feed system, and gas collection were tested and adjusted. Each of the three units was seeded with 2.5 liters of anaerobic digester sludge from the Bergen County Sewage Treatment Plant and fed a neutralized acetic acid substrate (20 g/l) at 15, 30 and 30 days detention time, respectively, for several days. Gas production and reduction in volatile acids indicated active units. The units were then fed neutralized foul condensate waste (batch 1) at 10, 20, and 20 days detention. The units did not respond. After two days, there was no gas production and the effluent COD was high. The reactors were emptied and restarted with fresh anaerobic digesting sludge and an acetic acid waste feed.

Figure 4-3, is a chronological record of the feeding, effluent COD and volatile acids concentration, and the gas production in Unit A. After 3 days of feeding neutralized waste at a 20 day detention, gas decreased and the feed was stopped. After an acetic acid feed and a gas response, indicating viability, the unit was fed a combined acetic acid/foul condensate waste, and the proportion of foul condensate was gradually increased. Gas production and effluent parameters (COD, volatile acids) were reasonably steady during this feeding schedule. The unit was then fed 100 percent waste at a 15 day detention. Gas dropped and effluent volatile acids and COD increased, as seen on day 40. Waste was fed intermittently until day 42, and fed daily to day 58 (except for 2 days). Gas production recovered and effluent volatile acids and COD concentrations returned to normal. Table 4-5 shows average results indicating over 90 percent COD reduction at a volumetric loading on the reactor of 0.9 kg/m^3-day. With the introduction of batch 2 waste, the unit was overfed, and pH dropped to 6.7. The pH in the reactor was adjusted to 7.3 and feed was withheld until gas production began to recover. After nine days, feed was resumed. Gas production increased during this period to the end of the study.

TABLE 4-5. SUMMARY OF SCREENING STUDY RESULTS

Unit	Feed; COD	Period Day No.	Detention Time Days	Loading kg COD/m^3-d	Effluent COD mg/1	Effluent VA mg/1	% COD_R	L Gas/ g COD_R
A Batch	Condensate No. 1 17.6 g/1	42-56	15	0.9	1630	892	90.4	.47
B Batch	Acetic Acid Control 20 g/1	56-72	10	1.9	465	560	97.7	.57
C Batch	Condensate No. 2 14 g/1	57-70	25-17	0.6	880	520	93.7	.51
D Upflow Bed	Condensate							
	No. 2 - 14 g/1	41-44	4.5	3.2	1280	750	90.9	.55
	No. 3 - 9.6 g/1	57-74	5.3	1.8	2910	1712	69.7	.94
E Anaerobic Filter	Condensate							
	No. 2 - 14 g/1	41-44	2.1	7.0	2020	1550	85.5	.59
	No. 3 - 9.6 g/1	57-74	2.1	4.6	3020	2060	68.5	1.0

Solids concentration in all reactors 1.5 to 2 percent.
Percent COD removal based on total influent, filtered effluent sample analyses.

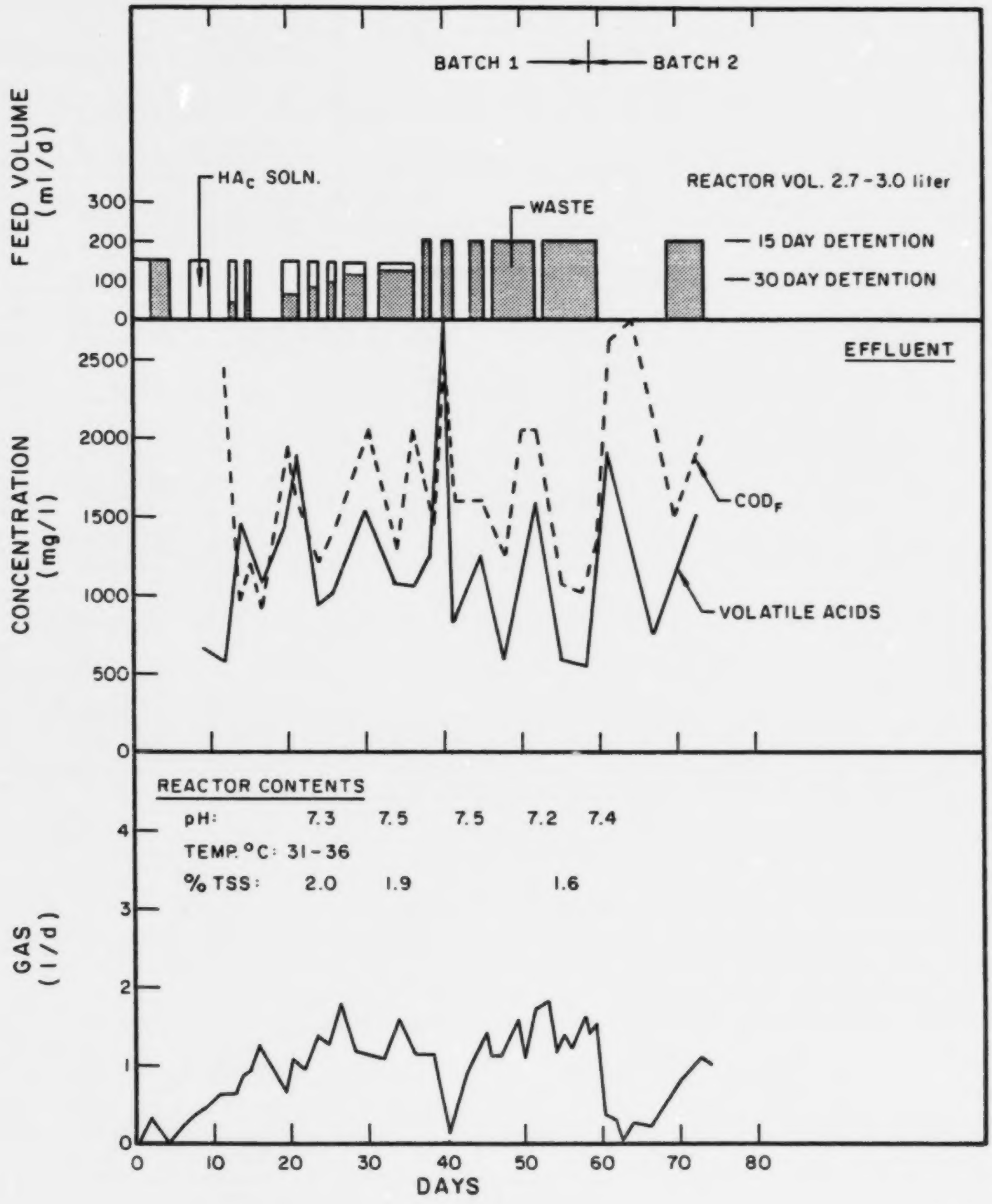


Figure 4-3. Screening study results for anaerobic batch reactor A.

Unit B results are shown on Figure 4-4. The unit was fed neutralized waste at a 10 day detention rate, and immediately gas production dropped and effluent volatile acids and COD increased. Feed was withheld for several days, then acetic acid was fed. After several days, gas began to be produced and effluent volatile acids decreased. The unit was fed waste again on day 21, and gas production again dropped off. Feed was stopped and practically no response was noted until acetic acid was fed intermittently. Gas production rose, and pH rose from 6.7 to 7.5 as volatile acids decreased. Waste was fed for one day and thereafter the unit was fed acetic acid at a 10 day detention to provide a comparison with units A and C. Table 4-5 indicates that a COD reduction of 97 percent was achieved during the steady state period during which only acetic acid was fed.

Unit C results are illustrated on Figure 4-5. Acclimation to the neutralized foul condensate without acetic acid addition was attempted in this unit. Initial feed was at a 10 day detention and, similarly to the other units, gas production dropped and effluent COD and volatile acids increased. Feed was withheld for several days, acetic acid was added on one day. After about 11 days, gas production increased markedly, COD_F and volatile acids decreased. The unit was then fed waste, and volatile acids and COD_F increased the next day, then decreased in subsequent days (gas measurements were not made due to a line leak during several days). Waste was then fed to the unit intermittently at a lower rate of 20 days detention. Gas production increased and effluent volatile acids and COD decreased. Waste was then fed daily (starting day 40) at a 30 day detention, until day 58 when detention was reduced to 25 days (Figure 4-5). Subsequently, the detention time was further reduced to about 20, then 17 days. Effluent COD and volatile acids were consistent and gas production responded to waste feed. Data in Table 4-5 indicate 93 percent COD removal during this period, and a typical gas production rate of 0.51 l/g COD removed.

The batch units data indicated the waste was treatable. Gradual acclimation to the waste, by an active digesting sludge could be achieved

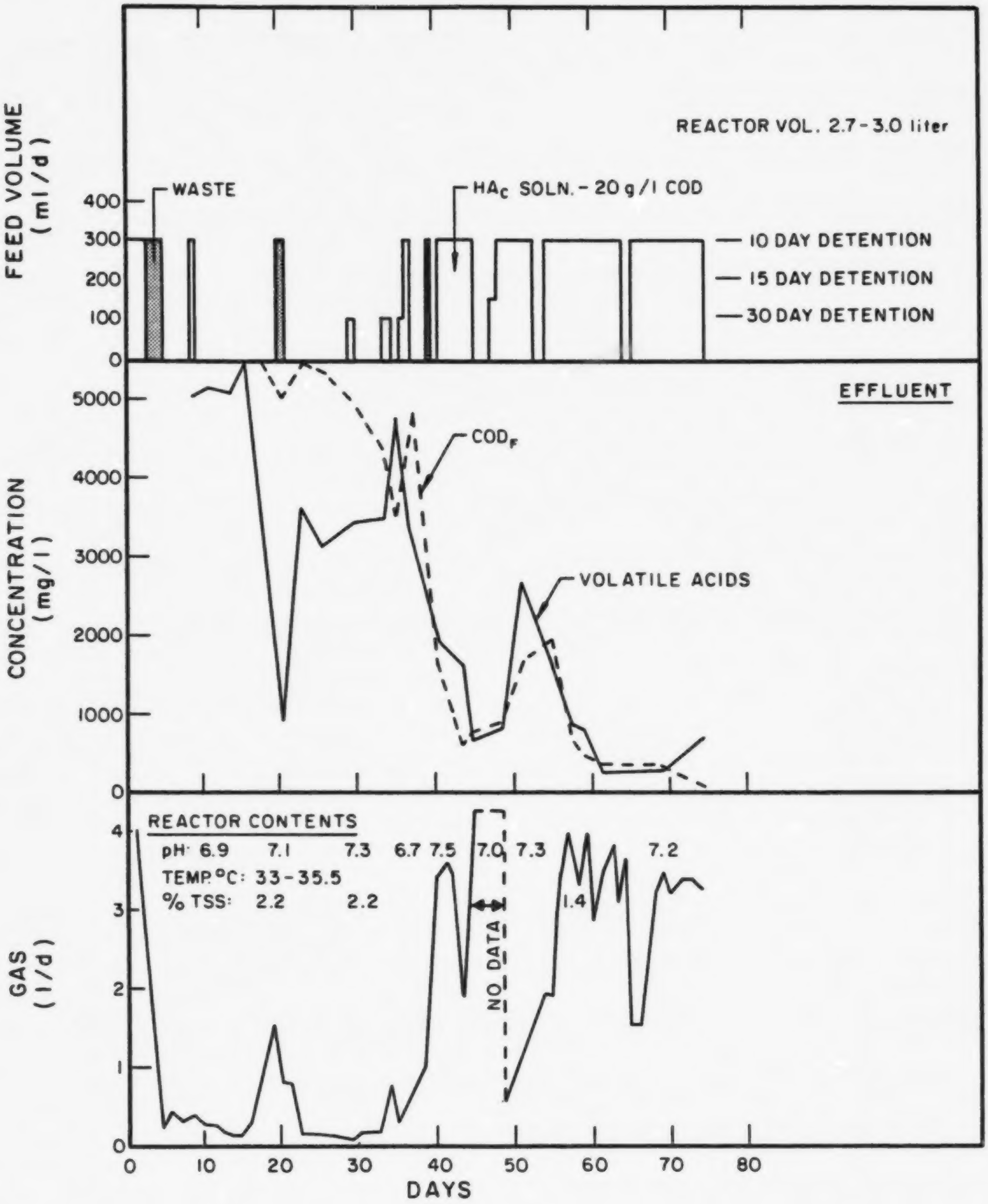


Figure 4-4. Screening study results for anaerobic batch reactor B.

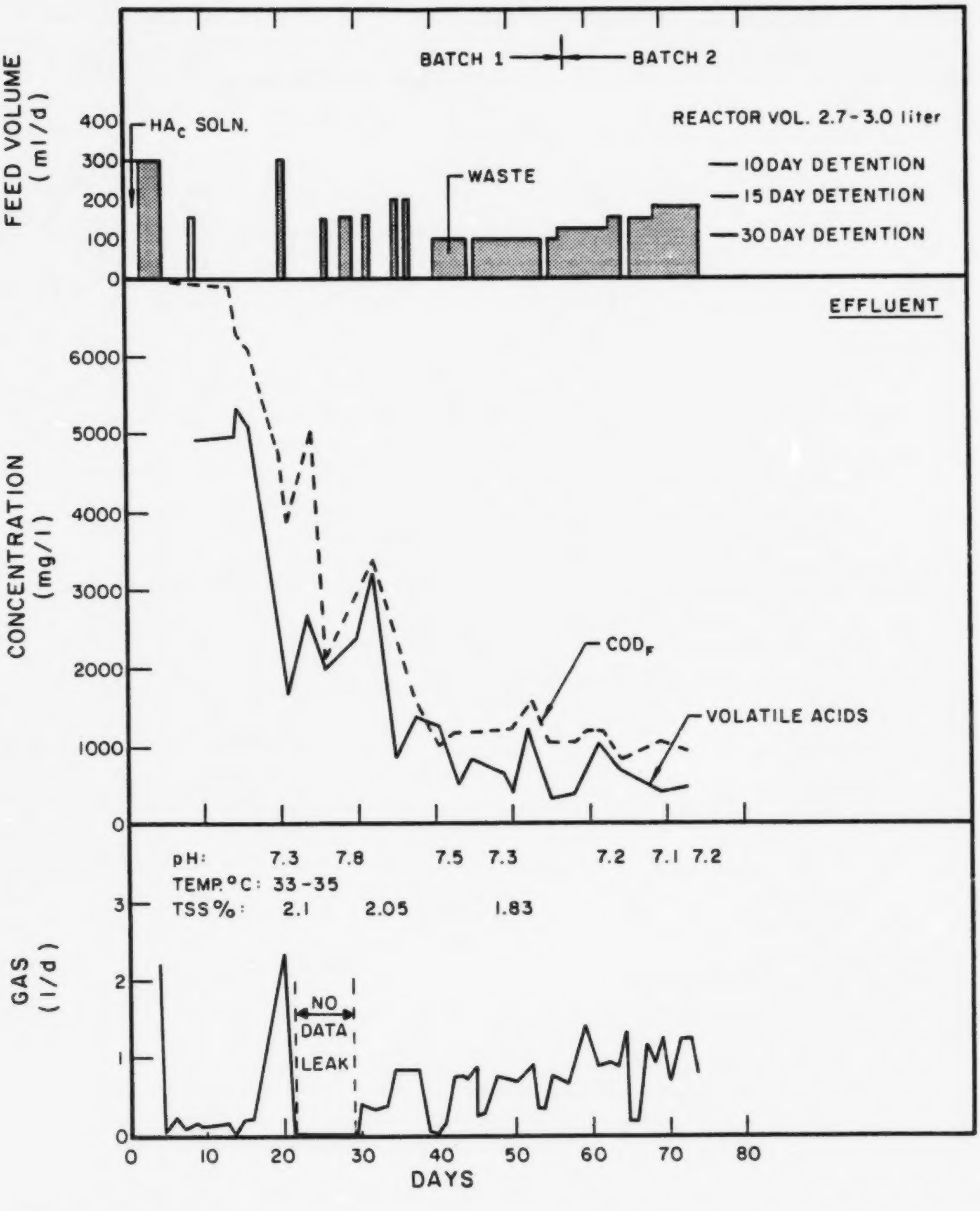


Figure 4-5. Screening study results for anaerobic batch reactor C.

in 30 to 40 days. Acclimation occurred by either gradually increasing the waste concentrations, as in Unit A, or by feeding once, and allowing sufficient time for the sludge to acclimate, followed by a gradual increase in feed rate, as in Unit C.

Continuous Flow Units

Unit D, operated as an upflow sludge bed unit, was seeded with two liters of digesting sludge. Unit E contained 5/8 inch pall rings which had been previously seeded during another anaerobic study; however, this unit had been inactive for several months. Unit E was seeded by adding 150 ml of effluent from the A batch reactor. Effluent was recirculated on both units at about 26 l/day. Influent was fed at rates varying from 0.2 to 2.0 l/day, depending upon the volumetric loading desired and waste COD concentration.

Figure 4-6 illustrates volumetric COD loading, effluent COD and volatile acids and gas production for the upflow sludge bed. Combined acetic acid substrate and foul condensate waste neutralized to pH 5.0, were fed to the unit. Initially, the loading feed rate was maintained constant and the percentage of foul condensate increased. The loading was gradually increased as was the percentage of foul condensate and by day 41, 100 percent waste at about 2.4 kg COD/m^3-d was being fed. Table 4-5 shows that 90 percent COD reduction was achieved, and normal gas production occurred for three days of operation during which loading had been increased to 3.2 kg/m^3-d. Unfortunately, the feed pump timer stuck, resulting in an excessive feed to the unit, which increased the loading to 5.8 kg/m^3-d. This resulted in a drop in pH to 4.7 and cessation of gas production. Alkalinity was added to raise the pH to 6.8 and the unit was reseeded with acclimated sludge from Unit C. After two days of recycling effluent, and no feed, waste feed was resumed (day 49). Effluent was recycled on day 50, feed added on 51, recycle only on 52 and 53, after which waste was fed continuously to the unit. The overloading experience prompted a decision to increase alkalinity addition to the raw waste by a factor of two, to about 5200 mg/l as $CaCO_3$, to minimize future low pH occurrences due to

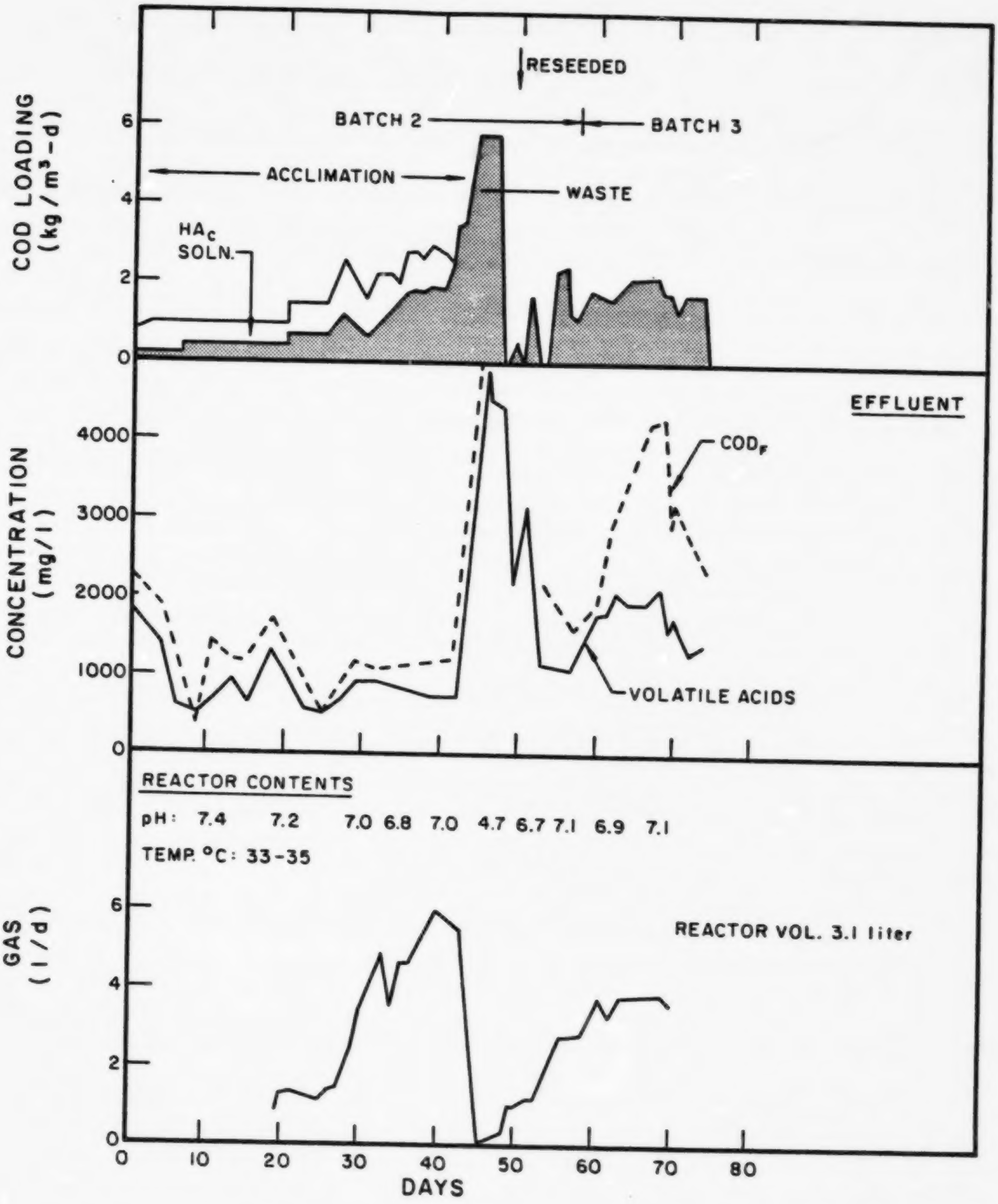


Figure 4-6. Screening study results for Unit D: continuous flow anaerobic upflow sludge bed.

similar experimental mishaps. The system recovered and gas production increased as shown on Figure 4-6. At an average loading of 1.8 kg/m^3-d, removals of about 70 percent of the COD were measured for day 57 to 74 as shown in Table 4-5.

The anaerobic filter, Unit E, was filled with an acetic acid solution, and put on recycle only. Volatile acids and COD_F decreased uniformly during the next 20 days (Figure 4-7), at which time influent waste feed was started. Initially, volatile acids increased in response to the increased loading. Over the following 30 days volatile acids gradually decreased to less than 500 mg/l, during which time loading and percent condensate waste fed to the unit were gradually increased up to 7 kg/m^3-d and 100 percent, respectively. As shown in Table 4-5, COD removal of 85 percent and gas production of 0.59 l/g COD removed were achieved at this loading. When the weaker waste, batch 3, came on line, loading dropped to about 4.6 kg/m^3-d. Consistent gas production was observed and effluent COD and volatile acids concentrations were decreasing toward the end of the screening study.

During the final eight days of operation of this unit, an experiment was conducted to determine if there was any acute inhibition due to higher concentrations of sulfites or sulfates in the waste. Two hundred mg/l of SO_4 was added to the feed to the unit for three days and 200 mg/l of SO_3 was added for the next five days. Gas production remained essentially constant during this period, and it was concluded that these higher concentrations of sulfate and sulfite would probably not be acutely detrimental to anaerobic treatment of the waste.

Toxicity Study

Following the procedure of Stukey,(1) a batch toxicity test was conducted from day 29 to day 41 using neutralized waste and both acclimated and unacclimated sludges from Units A and B. The purpose of this test was to determine if there was a waste concentration toxic to anaerobic degradation. The study was conducted since data in several references(2,3,4) indicated potential toxicity or inhibition of this type of waste

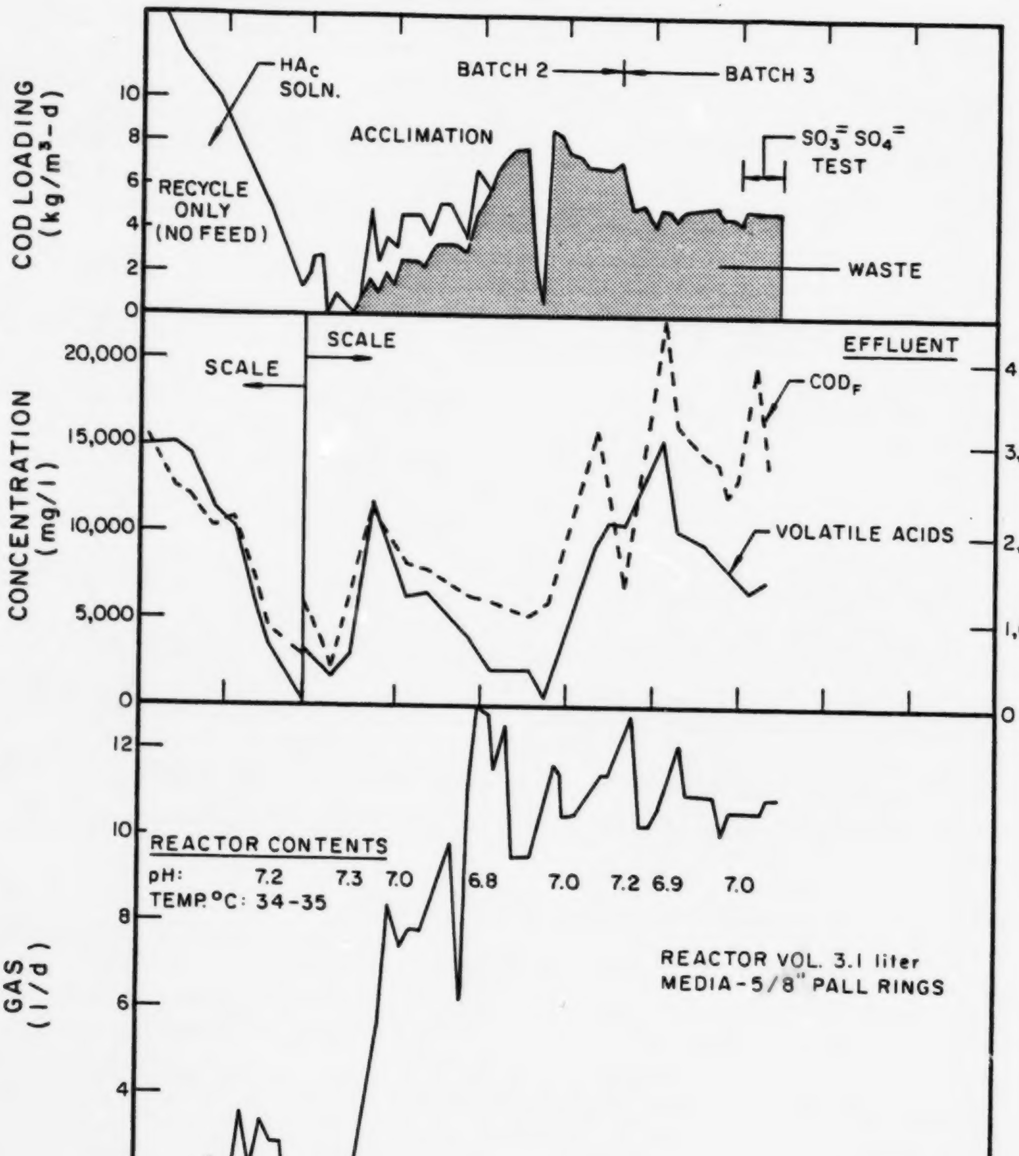


Figure 4-7. Screening study results for Unit E: continuous flow anaerobic filter.

to anaerobic treatment. Digesting sludge, 3 ml of acetic acid substrate, and varying amounts of the waste were added to 100 ml bottles, and were held at 35^{o}C. Gas was measured by displacement of a syringe volume over 12 days.

Test results with the unacclimated sludge indicated waste degradation, but were inconclusive. Gas production at waste concentrations of 3.3, 10, and 23 percent were close to 100 percent of theoretical, and gas produced at 1.7, 6.7, and 16.7 percent was below theoretical.

Test results using acclimated sludge were more consistent, as shown on Figure 4-8. No inhibition up to 23 percent waste by volume in the reactor was observed and gas produced was about 100 percent of theoretical. Inhibition, and gradual acclimation occurred at waste concentrations of 33 and 66 percent. These results indicated a probable need for acclimation of a seed sludge to the waste and potential inhibition to treatment at high waste concentrations.

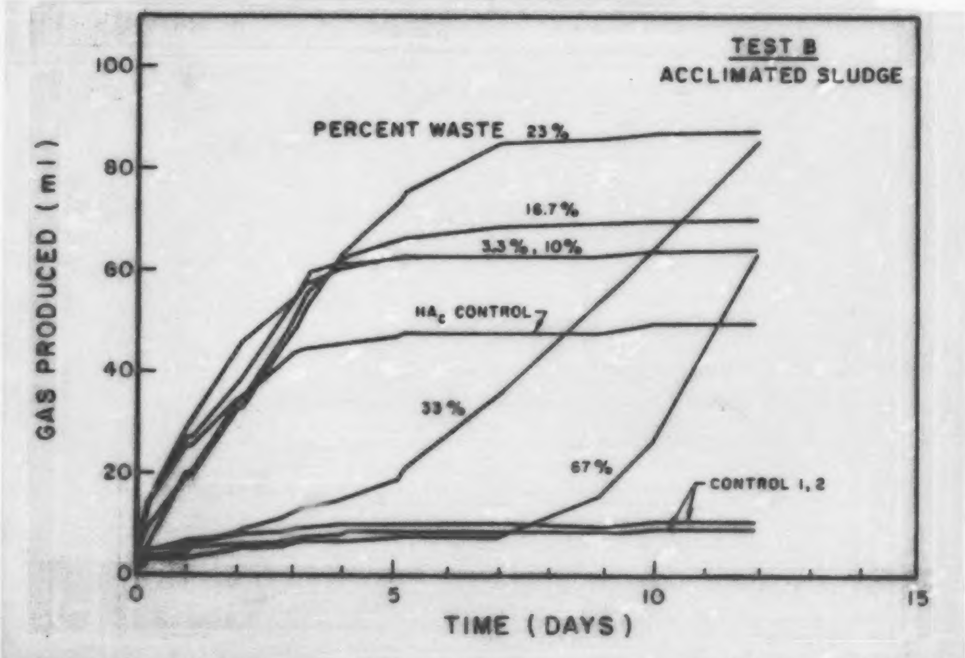


Figure 4-8. Batch toxicity test results.

This test and results of the batch reactors confirmed decisions t recirculate effluent in the continuously fed units to dilute influent concentration.

Analysis of samples, analytical procedures and quality assurance programs are discussed in another section. No particular problems were encountered with analysis for COD, alkalinity, pH, acidity, suspended solids, or the boiling titration(5) test used for volatile acids. Very limited testing was done for sulfur compounds, nitrogen, and BOD during the screening studies. Data from the screening studies are summarized in tables in the Appendix, Volume 2.

Summary

The screening studies clearly demonstrated that the waste was amenable to anaerobic treatment. Preliminary neutralization and nutrient requirements were determined based on waste characterization. Acclimation to the waste of a digesting sludge from a sewage plant was shown to be necessary and would require one to two months. Accordingly, it was decided to acclimate sludge prior to the pilot plant setup in order to accelerate startup and the achievement of the first loading period. The results of these studies tended to indicate a benefit of effluent recirculation in a continuous system, which was planned for in the pilot plant study. Familiarity with the analyses of the waste for COD and volatile acids, and a preliminary indication of possible effluent levels which could be achieved, were also developed during the screening studies. The laboratory studies were ended just prior to the pilot plant erection at the test site.

SECTION 5

PILOT PLANT FACILITIES

The three anaerobic technologies selected for evaluation included the upflow sludge blanket, filter, and fluidized bed. Manufacturers of the three technologies were contacted with respect to their recommendation on pilot scale design and sizing. The only recommendation received was for the fluidized bed. In this case, Dorr-Oliver and Ecolotrol, Inc. recommended use of a standard sized pilot unit for these studies, since it was their opinion that process scale up was feasible on the basis of results from these units. A design was developed for the anaerobic filter and upflow sludge blanket units, based upon previous experience with pilot plants and a meeting with Environment Canada personnel, to review their experience(1) with building and maintaining similar anaerobic pilot plants. The detailed designs of these pilot units were developed for the filter and upflow bed by IT Enviroscience, based on HydroQual's flow schematics and sizing data. The design and construction took under consideration the fact that these pilot plants were to be transportable. The two pilot plants were quite similar and could be utilized interchangeably and in other configurations, such as a downflow filter or a suspended growth system. Table 5-1 provides the basic sizing and design parameters of the three pilot plant systems.

The fluidized bed pilot plant was purchased from Dorr-Oliver, Inc. The unit was built specifically for this project, with only minor changes in their standard pilot plant unit to facilitate shipping, and to provide compatability with the pump units selected for the other two units. This type pilot plant had been utilized by both Dorr-Oliver and Ecolotrol on a number of anaerobic studies,(2,3) and was also utilized to provide design

TABLE 5-1. PILOT PLANT EQUIPMENT DATA

	Fluidized Bed	Anaerobic Filter	Upflow Blanket
Reactor material	Plastic	Steel	Steel
Reactor dimensions, m	3.65 x .15 ø	3.7 x .75ø	3.7 x .75 ø
Total volume in system, m^3	.065	1.55	1.55
Reactor volume,[a] m^3	.028 - .042	1.34	1.17
Feed pump var. speed, l/min	0 - 0.115	0 - 2	0 - 2
Recycle pump variable speed, l/min	0 to 23	0 to 19	0 to 19
Media description	0.3 - 0.6 mm sand	No. 3 FLEXI® rings (8.9cm)	None
Solids retention	Attached to media	Attached and suspended	Suspended
Solids blowdown	Remove from media	Drain	Drain
Clarification	None	None[b]	Internal settler[b]
Wet test gas meters, l/d	50 to > 15,000	50 to > 15,000	50 to > 15,000
Temperature control 35°C	Heating tape	3 kw heater, heat tape	3 kw heater, heat tape
Sampling ports spacing, cm.	30	30; 45	30; 45
pH control system	Yes	Yes	Yes
Buffer tank, l	4	100	100
Metering pump, l/min	0 - 0.4	0 - 0.4	0 - 0.4

Storage tanks stainless steel - 2 @ 4000 l with mixers.
Chemical feed tanks plastic 3 @ 100 l, one mixer.
Chemical feed meter pumps 3 @ 0 - 1 l/min.

[a] Effective volume based on media volume when operating, or depth to internal gas separation and settling zone in upflow blanket unit.

[b] External settling units provided for optional use.

parameters for scale up to full scale systems. Figure 5-1 is a schematic diagram of this unit. The reactor was 3.65 meters in height and 150 mm in diameter, and contained sand media 0.3 to 0.6 mm diameter at a fluidized height that ranged from about 1.5 meters to 2 meters, as growth was accumulated. There were sampling points at 30 cm spacing in the reactor column. A variable speed pump recycled effluent at about 9 l/min to fluidize the media. Waste was fed into the recycle line, utilizing a chemical feed pump. Temperature was automatically controlled with an electrical heater on the recycle line. A pH control system in which caustic feed to the recycle was controlled by a pH controller was included in the system. As biological growth developed, the reactor bed expanded, and at a selected depth (approximately 2 to 2.2 m) a portion of the media was removed through a port on the reactor column, cleaned and returned to the bed. Gas generated in the unit was separated from the effluent and was measured with a wet test meter before venting.

Components

1. Feed tank
2. Feed pump
3. Drain valve
4. Fluidized bed reactor
5. Sampling ports
6. Temperature controller
7. Heating tape
8. 3-way ball valve
9. Sand trap
10. Thermometer
11. Chemical feed tank and metering pump
12. pH probe
13. Recycle flow meter
14. Recycle pump
15. Gas sampling port
16. Gas relief valve
17. Gas-liquid separator
18. Foam separator
19. Gas flow meter
20. Siphon breaker
21. Control panel
22. Electric load center
23. Recycle pump controller
24. pH meter, controller
25. Timer
26. Electrical switches and outlets

Note:

® TRADE MARK DORR-OLIVER INC.

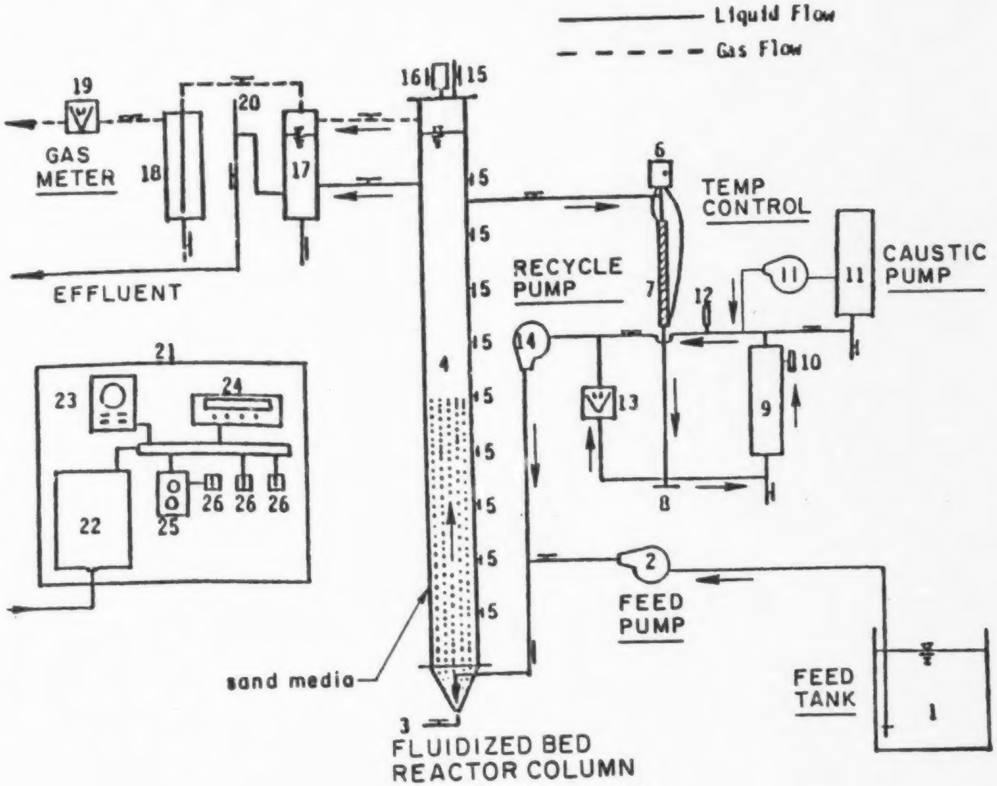

Liquid Flow
Gas Flow
19
GAS METER
18
20
17
EFFLUENT
16
15
5
4
6
TEMP CONTROL
RECYCLE PUMP
14
7
12
11
CAUSTIC PUMP
10
13
9
8
21
23
24
22
25
26
2
FEED PUMP
FEED TANK
1
sand media
3
FLUIDIZED BED REACTOR COLUMN

Figure 5-1. Schematic diagram of fluidized bed pilot plant.

Figure 5-2 is a schematic diagram of the anaerobic filter pilot plant. The steel reactor column was 3.7 meters tall and 75 cm in diameter. Media was supported by a screen above the influent baffle plate. A top screen retained the media, which was floatable, at a total depth of 305 cm. A heating tape was coiled around the column which was insulated to retain heat. Sample ports for liquid were located at 30 cm intervals in the bottom section and at 45 cm in the upper section. Three 15 cm diameter sample ports for obtaining media samples were located at media depths of 45, 106 and 228 cm. The type of media used in the column was 8.9 cm No. 3 Flexirings. The empty bed volume of the media zone was 1.34 m^3 and contained 1598 pieces of media resulting in a porosity of 97.2 percent with 85.5 square meters of surface area per cubic meter.

An adjustable level, removable cross weir was located above the media for effluent collection. Gas separated from the liquid in the column, passed through an outlet in the top of the column to a water trap and was measured by a wet test meter before venting. Effluent was discharged through a line which contained a pH meter probe and a sample pump tap.

A connection to the effluent weir permitted effluent recycle back to the unit influent, using a variable speed progressing cavity pump. Part of the recycle could be diverted to sprays on the top of the unit to knock down foam, if necessary. Rotometers were provided in the recycle and spray water lines to permit direct reading of flow rate.

A temperature sensor in the column was used to control a 3 kw electrical heater in series with the pilot unit influent and recycle flow line. Influent was fed to the unit using a variable speed progressing cavity pump. A timer control was used in conjunction with the pump for low flows. A rotometer on the influent line permitted direct reading of flow rate. Caustic solution could be added to the influent by use of a small metering pump, which could be controlled by the effluent pH indicator controller. During this study, this system was not used, since it was desired to maintain excess alkalinity in the waste for experimental and reliability reasons. Effluent sample pumps were provided to withdraw a sample from the

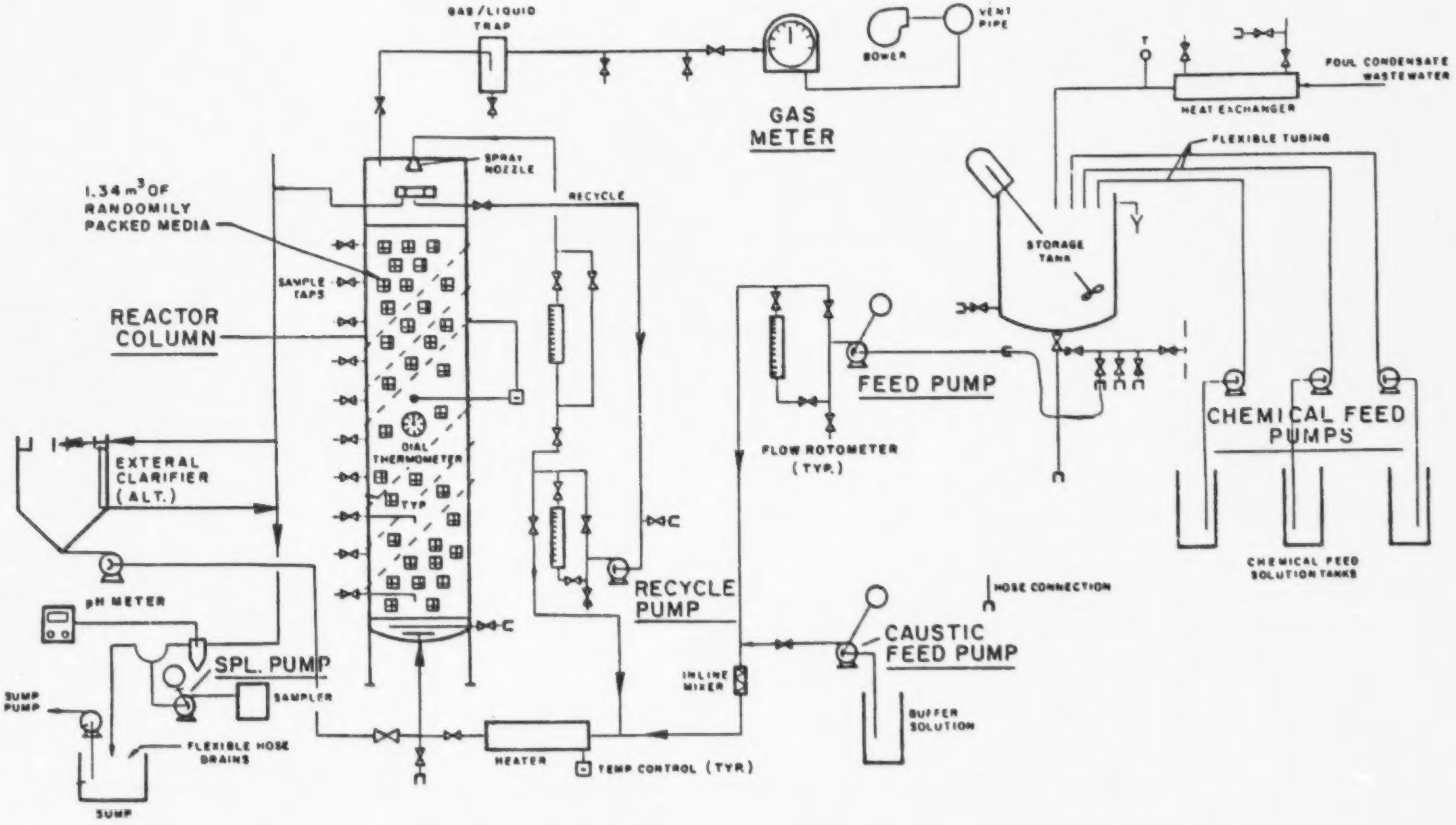

GAS/LIQUID TRAP
GAS METER
BOWER
VENT PIPE
FOUL CONDENSATE WASTEWATER
HEAT EXCHANGER
T
FLEXIBLE TUBING
SPRAY NOZZLE
RECYCLE
1.34 m³ OF RANDOMILY PACKED MEDIA
SAMPLE TAPS
REACTOR COLUMN
STORAGE TANK
Y
FEED PUMP
FLOW ROTOMETER (TYP.)
CHEMICAL FEED PUMPS
CHEMICAL FEED SOLUTION TANKS
DIAL THERMOMETER
TYP
EXTERAL CLARIFIER (ALT.)
RECYCLE PUMP
HOSE CONNECTION
CAUSTIC FEED PUMP
pH METER
SPL. PUMP
INLINE MIXER
SAMPLER
BUFFER SOLUTION
SUMP PUMP
FLEXIBLE HOSE DRAINS
HEATER
TEMP CONTROL (TYP.)
SUMP

Figure 5-2. Schematic diagram of anaerobic filter pilot plant.

effluent line to a container in a refrigerator. A clarifier on the effluent line was provided and used during certain periods of the study when it was desired to settle effluent solids and return them to the unit. A small positive displacement pump was used to return solids from the clarifier, to the reactor influent.

The upflow sludge blanket pilot plant schematic flow diagram is shown on Figure 5-3. The reactor had the same overall dimensions as the anaerobic filter, and had similar influent, recycle, chemical feed, heating, gas collection and sampling equipment. The unit, however, was built with an internal gas separation and solids clarification section above the sludge bed, as shown in the schematic. Gas from the sludge bed was diverted into the collection cone, while liquid flowed outside the cone to the collection weirs. A relatively quiescent zone was formed which allowed solids to settle and return to the sludge bed. The pilot plant was also supplied with an external clarifier for use with the reactor, to permit operation in the suspended growth anaerobic contact process mode. The clarifier also provided a backup for solids retention in the system in the event the internal clarifier performance was not adequate. The pilot unit was also supplied with gas recirculation capability which included a gas pump and a gas rotometer.

Two 4000 liter stainless steel tanks with mixers were provided with the pilot plants for raw waste collection, equalization, chemical addition, and feed storage. Three chemical feed tanks and metering pumps were provided to permit continuous or batch chemical addition to the raw waste.

An overall view of the assembled pilot facilites can be seen on Figure 5-4. Figure 5-5 shows the fluidized bed pilot unit in place with its steel frame for simplified erection and shipment. The anaerobic filter and upflow bed reactors are shown on Figure 5-6. Figure 5-7 shows a close up of the filter skid on which the recycle feed and chemical feed pumps, controls, pump timer control, heater, pressure gages, pH controller, chemical tank, flow meters, and electrical controls were mounted. Quick connections were used to connect the skid piping to plastic tubing leading

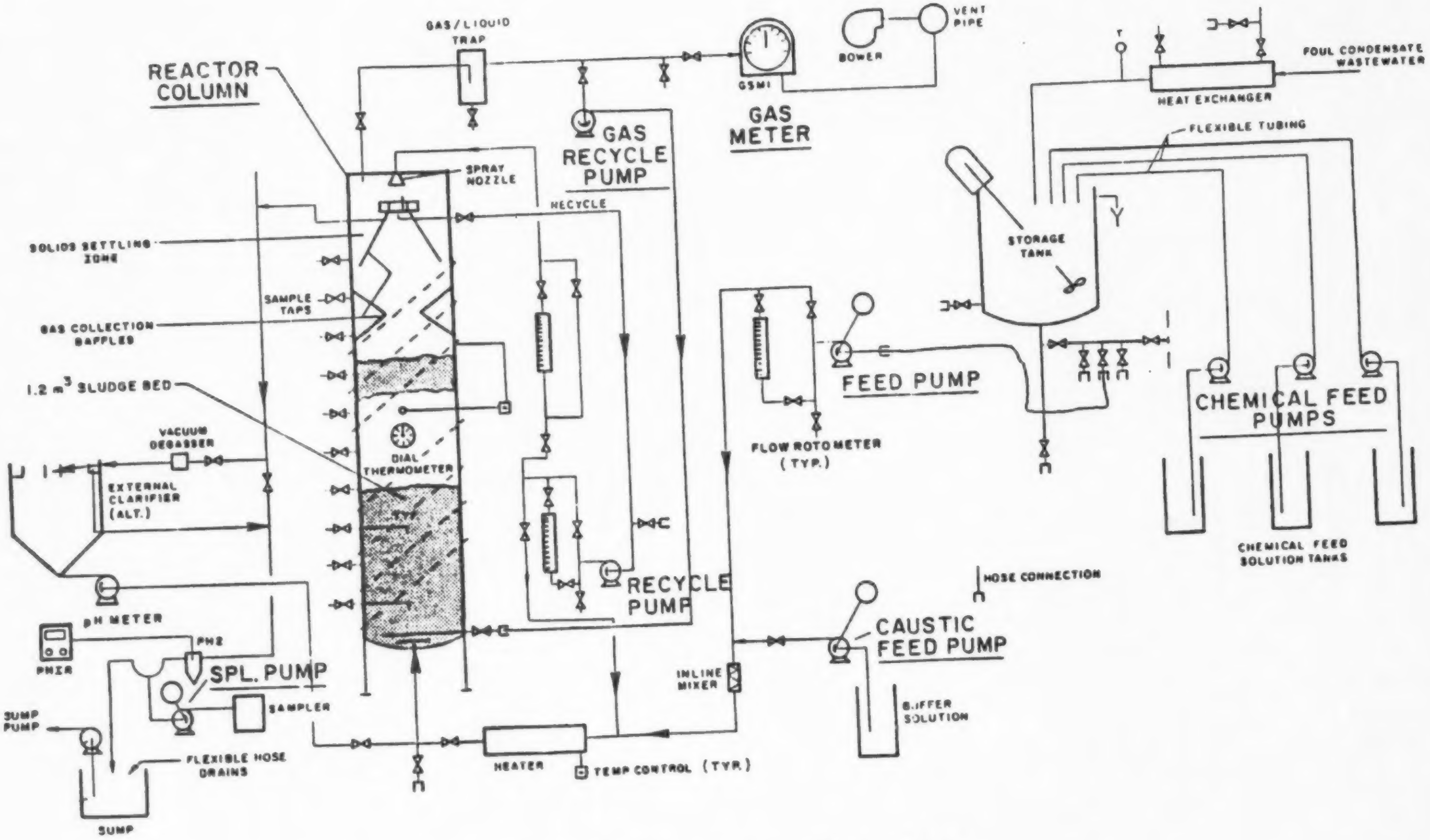

GAS/LIQUID TRAP
REACTOR COLUMN
GSMI
BOWER
VENT PIPE
GAS METER
GAS RECYCLE PUMP
SPRAY NOZZLE
RECYCLE
FOUL CONDENSATE WASTEWATER
HEAT EXCHANGER
FLEXIBLE TUBING
STORAGE TANK
T
SOLIDS SETTLING ZONE
SAMPLE TAPS
GAS COLLECTION BAFFLES
1.2 m³ SLUDGE BED
DIAL THERMOMETER
VACUUM DEGASSER
EXTERNAL CLARIFIER (ALT.)
FEED PUMP
FLOW ROTOMETER (TYP.)
CHEMICAL FEED PUMPS
CHEMICAL FEED SOLUTION TANKS
RECYCLE PUMP
HOSE CONNECTION
CAUSTIC FEED PUMP
pH METER
PH2
PHIR
SPL. PUMP
SAMPLER
SUMP PUMP
FLEXIBLE HOSE DRAINS
SUMP
INLINE MIXER
B.IFFER SOLUTION
HEATER
TEMP CONTROL (TYP.)

Figure 5-3. Schematic diagram of upflow sludge blanket pilot plant.

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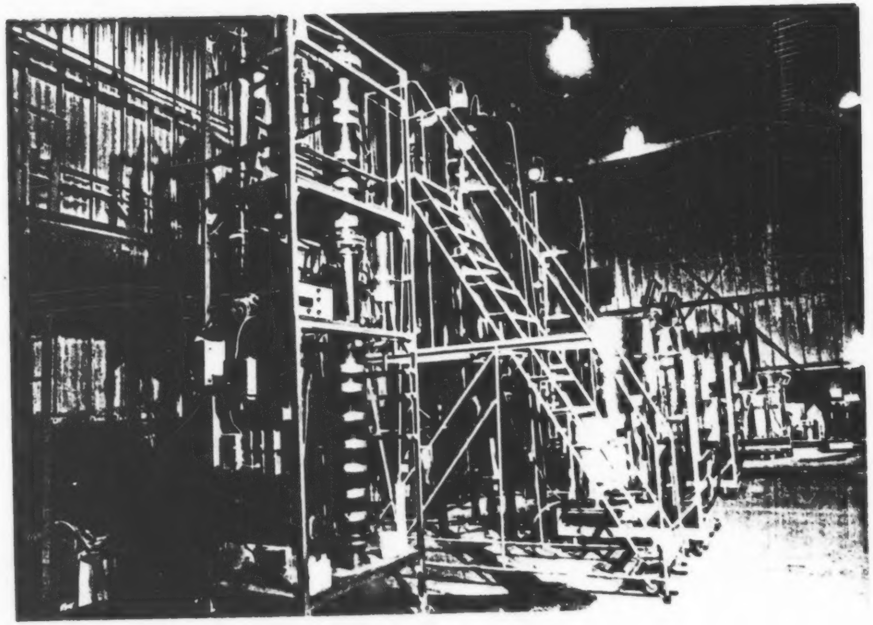

Figure 5-4. Pilot plants overall view.

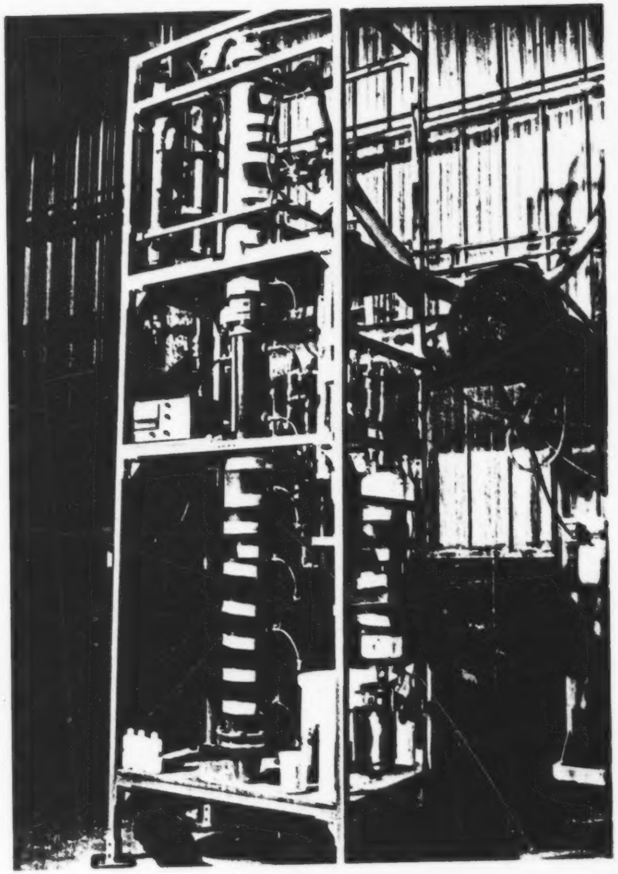

Figure 5-5. Fluidized bed.

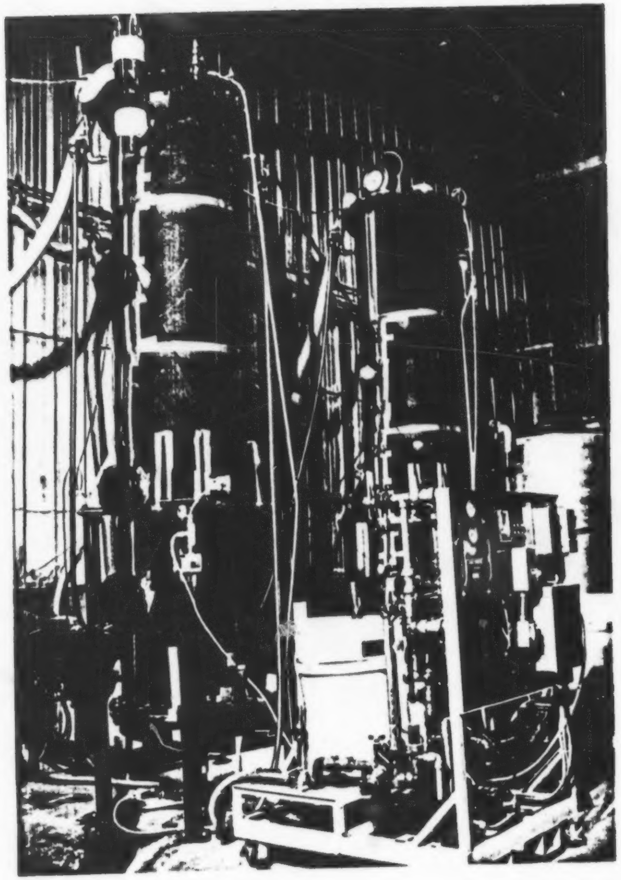

Figure 5-6. Anaerobic filter and upflow bed.

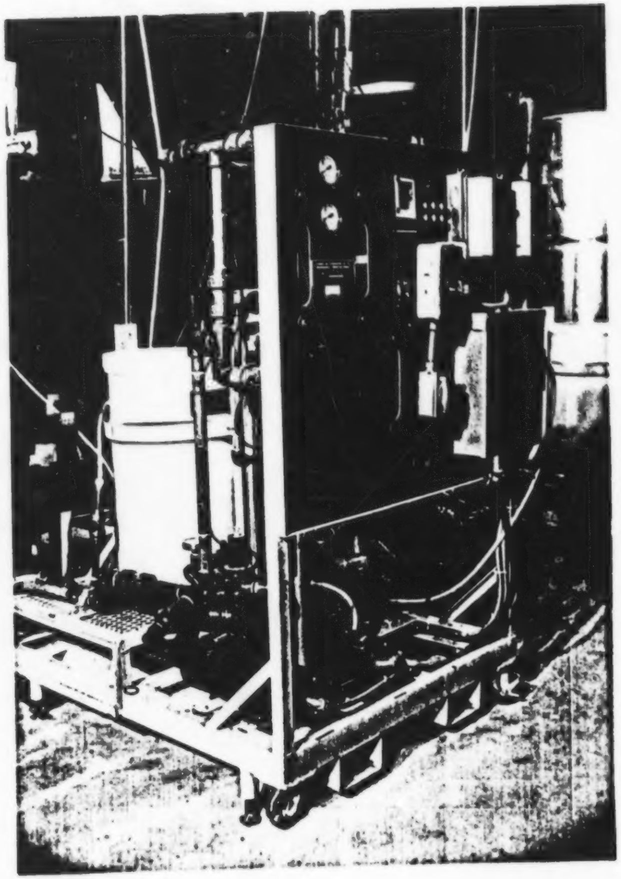

Figure 5-7. Filter control panel skid.

to the feed tanks and reactors. Figure 5-8 shows the two feed tanks and the skid mounted chemical feed tanks. Figure 5-9 shows the skid mounted sump and pump control which was required for this installation to pump effluent back to the industrial waste sewer. Also shown are clarifiers used on the filter and upflow blanket effluents. The sample refrigerator and sampling pumps can also be seen on this figure.

A skid mounted main electrical control panel provided for four main electric cables to each of the three pilot plant skids and the chemical feed skid, each of which had its own electrical circuit breaker control box. The power supplied to the pilot plants was 120V, 60 HZ.

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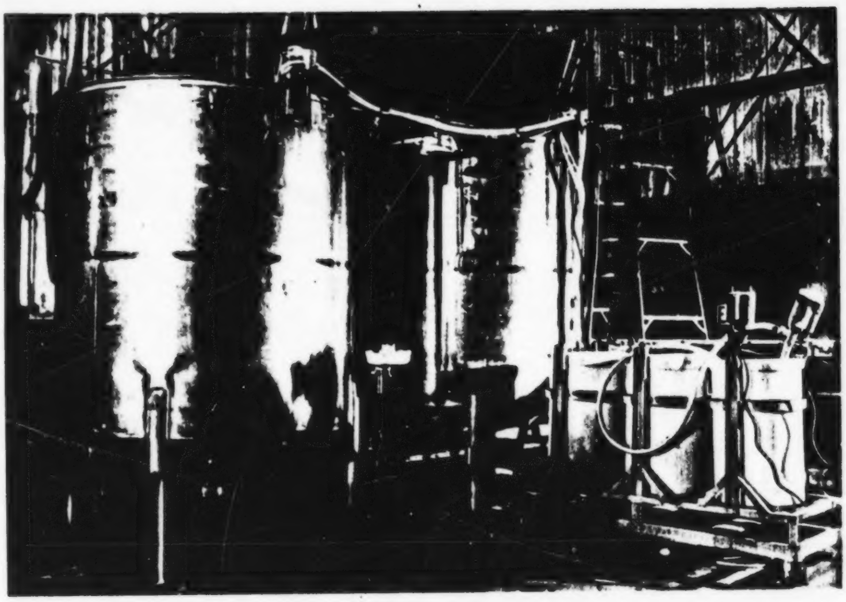


Figure 5-8. Raw waste storage and chemical addition.

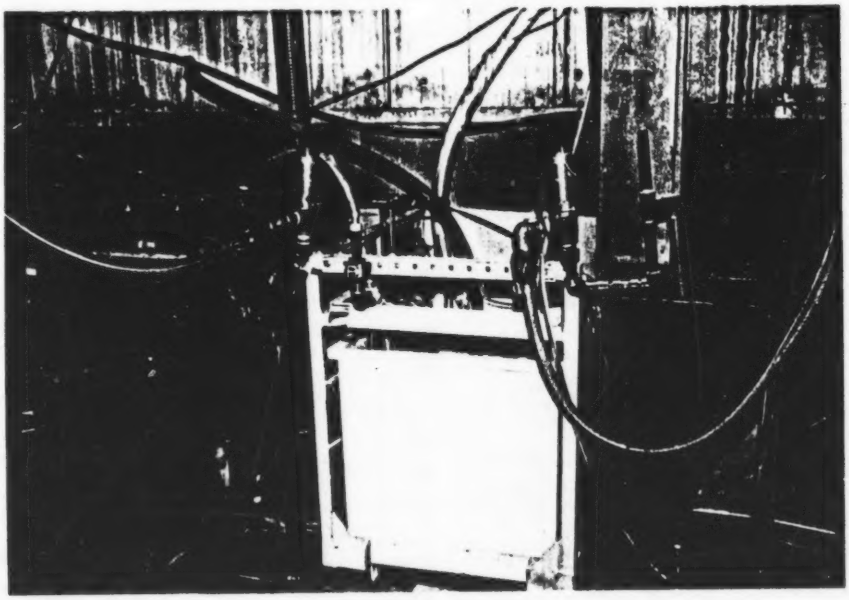


Figure 5-9. Effluent sump; final clarifiers.

SECTION 6

EXPERIMENTAL PLAN, MONITORING AND QUALITY ASSURANCE PROGRAM

INTRODUCTION

A quality assurance program was developed and approved for this project. The project was designed for the collection of performance data on a pilot scale, and was intended to evaluate and to perform assessments in a relatively unexplored area. The quality assurance level required was designed to produce scientific, but not legally defensible conclusions, and for data which would be valid on a relative, but not necessarily an absolute way to support technical evaluation. This section discusses the plan, the analytical and monitoring program, and summarizes results of the quality assurance program.

EXPERIMENTAL PLAN

An experimental plan was developed to meet the basic objectives of the study and to fit into the available time frame for the pilot plant studies. The plan was meant to be flexible and subject to change, based on results achieved as the studies progressed. Basically, the pilot plant program plan called for an initial startup period, increasing loading periods and operation at constant loadings at two or more levels. Special studies (tracers, spiking, tap sampling, and continuous variable flow) would be conducted as appropriate during the study.

Pre-Acclimation of Anaerobic Sludge and Media

The laboratory screening studies and information from others(1,2) indicated that significant time (one to three months) may be required to acclimate the anaerobic systems, before increasing loadings to the desired levels. Due to the limited study period, and in order to develop the pilot systems to reasonable loading levels in as short a time as possible, an acclimated sludge was developed during construction of the pilot plants. Anaerobic sludge from a well operating digester at a local treatment plant (Throop Borough, Pennsylvania) was collected and acclimated to the foul condensate waste. The fluidized bed media supplied with the pilot plant, had been previously seeded in a similar unit on an easily degradable synthetic waste.

Startup

The plan for startup was followed and is described below. The pilot systems after setup were initially operated on tap water to ensure that there were no leaks and they were in working order. Gas (air) was purged into the units to check for gas tightness and the functioning of the gas measurement equipment. The initial testing of the fluidized bed was conducted at Dorr-Oliver before shipping, and the system was ready for startup after delivery and hookup at the site.

The media was then added to the anaerobic filter and the fluidized bed pilot units. The acclimated sludge was added to the anaerobic filter and upflow sludge blanket units. Supernatent from the acclimated sludge was used to fill the fluidized bed system. Additional volume was made up with neutralized waste to fill the systems. The pilot plants were then operated on a recycle mode. After volatile acid levels decreased, neutralized waste was fed to each pilot unit at a low rate. Based on analyses of COD removal and effluent volatile acid concentration, feed rates were adjusted upward to the extent that effluent volatile acid concentrations between 1000 and 3000 mg/l, and COD removals between 60 to 75 percent were maintained. As the systems exhibited increased removals, loading was increased by increasing the feed rate. This procedure was planned to be continued during the first two months of the study, or until the desired loading rate, at which steady state operation was to be analyzed, was reached. During acclimation, the raw waste was collected on an as-needed basis and prepared by neutralization and nutrient addition as indicated in Table 4-3.

Loading Conditions

After acclimation and attainment of COD removals over 70 percent, and effluent volatile acids below 2000 mg/l, it was planned to impose a constant influent feed rate at a selected loading rate on each of the pilot units. The pilot units would be operated at the loading condition for about two months, or until a relatively steady state condition was reached. Steady state was defined as a constant removal rate at constant loading for about two weeks. The feed rate would then be increased gradually over a period of several days or more, using the previously established procedure as a guide, to achieve the next loading rate to be studied.

The study program called for investigation of at least two loading conditions. Depending upon each system's rate of development, additional higher loading conditions would be studied. Approximate loading rate targets hoped to be achieved during acclimation and the loading conditions are indicated in Table 6-1 for each of the systems.

TABLE 6-1. PRELIMINARY LOADING RATE GOALS kg COD/m^3-d

Pilot System	Minimum Loading	First Loading Period (2 months)	Second Loading Period (2 months)	Probable Maximum Loading[a]
Anaerobic filter	5	5 to 10	15 to 20	25 to 35
Upflow bed	5	5 to 10	10 to 20	20 to 25
Fluidized bed	5	10 to 15	15 to 25	20 to 30

[a] Based on references cited in Section 3.

The plan called for operating at these loading rates and achieving COD removals of 70 to 90 percent for at least two weeks. This would permit collection of a reasonable amount of operating data and sample analyses.

Table 6-2 lists the actual time periods selected for data analysis for each of the pilot plants, and the average loading during the period. The three pilot plants were all operated during the same initial period at about the same loading rate.

TABLE 6-2. DATA ANALYSIS PERIODS AND AVERAGE LOADINGS TO PILOT PLANTS

Pilot Plant	Period (Day to Day)	Average COD Loading kg/m^3-d
Filter	46 - 69	7.2
	143 - 158	11.1
	164 - 179	16.5
	187 - 207[a]	24.8
Upflow Sludge Bed	46 - 69	6.7
	129 - 179	4.9
	183 - 202	4.4
Fluidized Bed	46 - 69	6.1
	97 - 124	24.0
	145 - 155	17.0
	156 - 166	25.0
	168 - 179	35.0
	193 - 198	102.0
	202 - 207	64.0

[a] Includes half depth study period.

Thereafter, the periods selected differed based on pilot plant performance. Periods of consecutive days at a given condition were selected for data analysis and comparison, and were based on data and each pilot plant's operating conditions. Periods during which time an upset or a recovery situation occurred, were not included, nor were periods including days with zero or exceptionally high loadings, which would tend to distort averaged data. Although some periods were shorter than the planned two weeks, generally, each period reflected a fairly constant loading and removal condition. There were variations about the average removal and loading during each period, however, there were no significant increasing or decreasing trends with time. The results from each of these periods are presented and discussed further in Sections 7 and 8.

Obviously, some of the periods are less than the two week period for data analysis at a steady state condition hoped for in the project plan; nevertheless, the data during these periods were valid, and reflective of the results under the specific operating conditions. The shorter periods, particularly with the fluidized bed, occurred at the higher loading rates at shorter detention times and during which increased sample analyses were obtained. The question of attainment of a steady state condition is discussed with the data in Sections 7 and 8.

Tracer Studies

Tracer studies were conducted on the pilot units at several times during the study. A lithium chloride tracer was used to determine the hydraulic characteristics of the pilot systems (plug flow, complete mix or partial complete mix). The tracer was injected into the feed line and samples collected over a sufficient period to characterize the system.

Depth Studies

During several loading conditions, samples were taken from each pilot unit at various depths in the units to determine removal patterns and suspended solids content.

The anaerobic filter was drained and sampled at incremental depths, and media were sampled to determine both suspended and attached biological mass within the pilot unit at the end of the study. The fluidized bed unit was sampled to determine attached growth, and the upflow sludge blanket bed was sampled at depths to determine suspended growth at the conclusion of the study.

Other Studies

The foul condensate waste was collected during full operation of the evaporator. For one to two hours per shift an evaporator compartment is washed resulting in carry over of sulfite liquor into the condensate. To determine if this would have a significant effect on treatment, a short study was conducted on the fluidized bed unit at the end of the study. A simulated 24 hour waste which included sulfite liquor carryover was fed to the pilot plant.

A continuous period of operation and continuous condensate flow to the equalization tank was planned, if time permitted. Based on data collected on the observed variability of loadings and the fairly consistent characteristics of the condensate, this program was not felt to be necessary to obtaining design information, and was not conducted.

SAMPLING AND MONITORING PROGRAM

During acclimation, sampling and analyses was limited to the degree needed to bring the systems up to loading and provide information on the units overall performance. In general, monitoring concentrated on gas production, COD removal, volatile acids, pH and alkalinity.

During the loading condition studies, sampling and analyses frequency was increased to the extent needed to define the performance of the units. Samples were collected, and analyses conducted on the various parameters to permit development of design and operating data.

Table 6-3 outlines the actual sampling frequency and analyses conducted for acclimation periods and loading periods during the study. Table 6-4 indicates daily data collection from the pilot plants. All data were recorded on daily log sheets, and sample analysis data were recorded on standard laboratory data sheets. Data were then transcribed to summary data sheets. Print outs of the data are reproduced in the Appendix of this report.

TABLE 6-3. PILOT PLANT ROUTINE MONITORING SCHEDULE

Analysis	Frequency times/week Raw Waste	Influent	Effluents (3 units)
pH	(1)	Daily	Daily
Acidity/Alkalinity	(1)	Daily	Daily
COD_T	up to 3	3	3
COD_F	–	1	1
BOD_T	(1)	1	1
BOD_F	–	1	1
TOC	–	1	1
TS	–	1	1
TVS	–	1	1
SS	–	3	3
VSS	–	1	3
SO_4	–	1	1
SO_3	–	1	1
H_2S-S	–	1	1
PO_4-P	–	1	1
NH_3-N	–	1	1
TKN	–	1	1
Volatile Acids	(1)	Daily-3	Daily-3
Color	(1)	3	3

(1) A raw waste sample of each batch was collected and analyzed as indicated.
Gas analyses three times/week - CH_4, CO_2.
T-Total sample analyzed.
F-Filtered sample analyzed (0.45 micron glass fiber filter).

TABLE 6-4. PILOT PLANT DAILY DATA COLLECTION

System Parameters

- Time of Observations
- pH/Effluent
- Flow: (note time and flow adjustement if any)
  - Waste
  - Recycle
- Temperature
- Gas Production and Rates

Raw Waste Neutralization/Nutrient Feed

- Volume Transferred to Tank
- pH
- Acidity
- Alkalinity Added (Type, Quantity)
- Resulting pH
- Nutrients Added
  - Nitrogen
  - Phosphorus
  - Trace (See Table 4-3)

List personnel on site.
Describe any malfunctions or problems and corrective actions.
Describe any special testing conducted.

Analytical Program

The planned analytical schedule was generally followed; however, a number of changes were made as the project progressed. The pH, alkalinity, volatile acids, and TOC were run five to seven times per week. Total organic carbon (TOC) was determined by the difference between measured total carbon (TC), and total inorganic carbon (TIC). Volatile organic acids (VOA) were measured as acetic acid. Analyses of samples for filtered COD was changed from twice per week to daily during the final month of the study. TKN and ammonia nitrogen analyses were performed once every two to four weeks for certain periods during the study due to time constraints and actual need for these analyses. Gas analyses for CO_2 and CH_4 were not performed during the first two months due to delays in obtaining necessary parts for the gas chromatograph. A few analyses using an Orsat test kit were conducted initially.

Routine analyses were determined on site in a mobile laboratory facility, except for ammonia and TKN. During the study, it was determined that results for ammonia and TKN utilizing the micro-apparatus installed in the mobile laboratory was extremely time consuming and did not always meet quality assurance goals. Accordingly, samples were prepared for this analysis, and the analyses were conducted at our laboratory by the field chemist using a standard multiple Kjeldhal apparatus.

Table 6-5 presents the quality objectives set for analyses, and the reference for analytical procedures. The procedures used were approved USEPA procedures following "Standard Methods for the Examination of Water and Wastewater," 15th Edition, and/or standard recommended methods for the specific instrumentation used. Volatile acids were determined by a quick titration test procedure as described by DiLallo and Albertson.(3) It was not practical to use the gas chromatographic equipment on a routine basis for volatile acids due to apparent rapid fouling of the columns with this waste. Hydrogen sulfide measurements were not made with the gas chromatograph since the necessary columns were not available to this project. Several analyses of hydrogen sulfide contained in the gas were

TABLE 6-5. QUALITY OBJECTIVES FOR MEASUREMENT DATA

MEASUREMENT METHOD	REFERENCE[a]	ADDITIONAL TEST CONDITIONS	REPLICATES PRECISION WITHIN CONTROL LIMITS	SPIKES ACCURACY	QA ANALYSES COMPLETED
DISSOLVED OXYGEN PROBE METHOD	421F	PROBE CALIBRATED AGAINST WINKLER TITRATION	N/A	N/A	90%
pH, UNITS pH METER (ELECTRO)	423	-	N/A	N/A	90%
CHEMICAL OXYGEN DEMAND (mg/1) DICHROMATE, REFLUX	508A	ACIDIFY SAMPLE	90%	90%	90%
ALKALINITY, mg/1 $CaCO_3$ ELECTROMETRIC ENDPOINT	403	-	N/A	N/A	90%
TOTAL SUSPENDED SOLIDS (mg/1) GRAVIMETRIC	209D	-	90%	N/A	90%
VOLATILE SUSPENDED SOLIDS (mg/1) GRAVIMETRIC	209G	-	90%	N/A	90%
TOTAL SOLIDS (mg/1) GRAVIMETRIC	209A	-	90%	N/A	90%
TOTAL DISSOLVED SOLIDS (mg/1) GRAVIMETRIC	209B	-	90%	N/A	90%
BIOCHEMICAL OXYGEN DEMAND (mg/1) 5 DAY - 20°C	507	DO MEASUREMENTS BY PROBE METHOD	90%	90%	90%
TOTAL CARBON, INORGANIC CARBON (mg/1) DIRECT INJECTION INFRARED		MANUFACTURERS RECOMMENDATION	90%	90%	90%
SULFATES (mg/1)	426-C	COLOR COMPENSATE	90%	90%	90%
SULFIDES (mg/1)	427/AFTER PURGING FROM ACIDIFIED SAMPLE	PURGE ACIDIFIED SAMPLE INTO ZINC ACETATE	N/A	N/A	90%
SULFITE (mg/1)	428	-	N/A	N/A	N/A
GAS COMPOSITION (mg/1)	GC METHOD	GAS SAMPLING TUBES, TC DETECTOR FOR CO_2, METHANE	85%	80%	90%
VOLATILE ACIDS (mg/1) BY GC	GC METHODS	FID DETECTOR BEFORE AND AFTER DISTILLATION	80%	80%	80%
VOLATILE ACIDS mg/1 BY TITRATION	504A; DIRECT TITRATION METHOD (REF. 58)		80% 80%	80% 80%	90% 90%
TOTAL KJEHLDAL NITROGEN (mg/1) MANUAL METHOD	420-B/SEMI MKRO WITH NH_3-N PROBE	ACIDIFY MICRO REFLUX AND DISTILLATION TITRATION	90%	90%	90%
AMMONIA NITROGEN (mg/1) DISTILLATION METHOD	417-B AFTER MICRO DISTILLATION TITRATION	ACIDIFY SAMPLE	90%	90%	90%
PHOSPHORUS	424D	-	90%	90%	90%
LITHIUM	ATOMIC ADSORPTION TECHNIQUES	-	90%	90%	90%

[a] STANDARD METHODS FOR THE EXAMINATION OF WATER AND WASTEWATER 15TH EDITION.

made on samples towards the end of the study using hydrogen sulfide detection tubes from Mine Safety and Appliances Company. Estimates of hydrogen sulfide concentrations in the gas were calculated on the basis of sulfide and pH measurements of the reactor contents.

In order to properly assess the results and performance of the pilot study, the type analysis being conducted and the concentration levels present did not require a high degree of accuracy or precision. To ensure that the measurements being made were reasonably accurate, the field personnel who performed the analyses, were thoroughly trained in each of the test procedures during the screening studies, and at the mobile laboratory by the quality control officer and laboratory staff members. In addition, the following program generally was followed for analyses to ensure data precision and accuracy of analysis.

For critical analyses:

- BOD, COD, volatile acids, TOC, solids (replicate only)
- One influent and one effluent sample each week analyzed in duplicate.
- One influent and one effluent sample each week spiked for recovery analyses.

For less critical and infrequent analyses:

- PO_4-P, SO_4, SO_3 (replicate), TKN, NH_4-N
- One influent and one effluent sample each month analyzed in duplicate.
- One influent and one effluent sample each month spiked for recovery analysis.

- Samples selected on alternating weeks of each month, rotating effluent samples selected.

As part of all routine instrument analyses, both blanks and standards were performed with each sample run. The concentration range of the standards were sufficient to bracket sample values.

The USEPA reference samples (Environmental Monitoring and Support Laboratory, Cincinnati) were analyzed for applicable parameters during the project.

During the project, the field engineer and the project director reviewed pilot plant and analytical data as it was being generated, at least once a week. Daily spiking and review of recovery on COD analyses were conducted and any apparent data anomaly was questioned and causes or reasons for it were investigated. Apparent outlier analytical data was identified and, if possible, the sample was reanalyzed. Samples after analyses were generally retained under refrigeration for two to three weeks, and some were stored in the mobile laboratory unheated storage bay, without refrigeration for up to six weeks during the colder months of the study, to permit reruns if required.

The results of the Quality Assurance Analytical Program are included in the Appendix with a discussion of the results of each analysis. A summary is presented in Table 6-6. Quality control limits for analytical results were based on three standard deviations. Results of the analyses were compared to these limits, as shown in the table. Except for TKN and ammonia nitrogen analyses performed at the mobile laboratory as previously discussed, the analyses met the quality control objectives outlined in Table 6-5.

TABLE 6-6. QUALITY CONTROL DATA
SUMMARY OF SPIKE RECOVERY, REPLICATES AND STANDARD ANALYSIS

A. Spike Recovery Analyses

Parameters	Number	Average Recovery %	Standard Deviation	Control Limits[a]	% Samples Within Control Limits	% Completed
Volatile Acids	9	95.2	2.8	8.4	90	30
BOD_5 (standard)	44	102.8	8.5	26.0	100	100
COD	53	98.8	5.0	15.0	100	100
TIC	24	103.0	15.4	46.2	100	83
TC	26	103.0	21.4	64.2	100	83
Ammonia-N	6	83.0	13.3	39.9	100	42
TKN-N	14	93.1	15.7	47.1	100	100
PO_4	13	99.8	20.3	60.6	100	92
Sulfate	28	101.5	14.8	44.4	100	100

B. Replicates Analyses

Parameters	Number	Average Recovery[b] %	Standard Deviation	Control Limits[a]	% Samples Within Control Limits	% Completed
Volatile Acids	134	1.57	1.53	4.59	95	100
BOD_5 (standard)	21	1.5	1.2	3.6	95	70
COD	38	1.14	1.23	3.69	90	100
Ammonia-N	5	4.18	5.05	15.2	100	35
TKN-N	12	3.4	3.4	10.2	75	86
PO_4	12	1.39	1.28	3.84	92	85
Sulfide	34	5.6	4.0	12.0	97	100
Sulfite	35	2.1	1.25	3.75	94	100
Sulfate	32	3.36	4.0	12.0	97	100
TS	29	1.03	1.5	4.5	93	100
TVS	28	2.9	2.1	6.3	96	100
SS	85	5.8	5.7	14.1	93	100
VSS	59	5.3	4.9	14.9	95	
Gas Analysis						
CH_4	88	0.15	0.16	0.48	96	N/A
CO_2	88	0.36	0.36	1.08	94	N/A

C. Recovery Analysis for Standards

Parameter	Number	Average Recovery %	Standard Deviation
Volatile Acids	15	99.7	3.4
BOD	20	107.0	7.4
COD (Standard)	8	99.1	2.7
(USEPA Standard)	6	101.0	1.8
TIC USEPA Standard	3	105.0	17.0
TC USEPA Standard	3	82.7	2.3

[a] Three times standard deviation.

[b] $i = \frac{A-B}{A+B}$ (for duplicate samples).

SECTION 7

PILOT PLANT PROGRAM RESULTS

This section presents the chronological results of the pilot plant operations and data collection. The raw and neutralized wastewater characteristics are presented. Pilot plant startup and operation are described and discussed. Data during the loading periods are summarized, and a summary design relationship of COD loading and removal efficiency comparing the performance of the pilot plants is presented.

WASTEWATER CHARACTERISTICS

During the course of the pilot plant studies, 47 batches of foul condensate were collected. The condensate was collected during full operation of the evaporator, excluding wash periods. During the early part of the study, samples of foul condensate had COD values considerably less than preliminary data indicated. It was discovered that a plant process change at the evaporator required addition of cooling water to the condensate for pressure control within the evaporator. When this was determined, samples of foul condensate starting with batch 16, day 70, were normally collected while the cooling water was turned off. This resulted in higher, more uniform wastewater concentrations, except for several occassions.

Figure 7-1 illustrates raw waste characteristics and variations. The effect of the dilution water on COD concentration can be seen from day 50 to 70. Color was generally less than 50 units. The acidity of the waste varied, reflecting acetic acid concentration and the dilution. Some of the

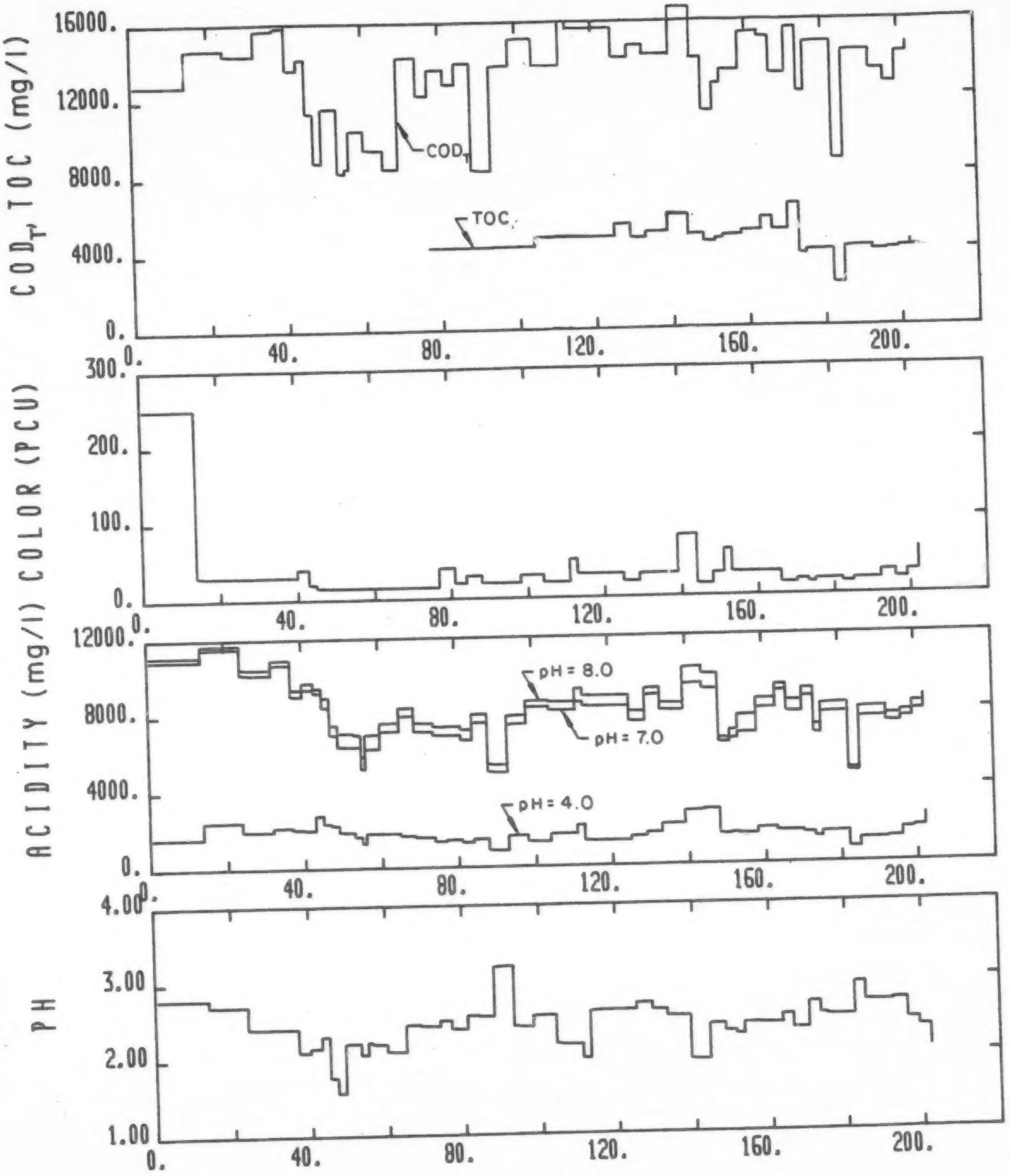


Figure 7-1. Foul condensate waste characteristics.

acidity to pH 4.0 can be attributed to sulfur compounds, since the minimum pH of an acetic acid solution at these concentrations is in the range of 2.8 to 3.0.

Table 7-1 presents the results of the analysis conducted on raw waste, showing the range and average values. The average COD for batchs 1 to 7 and 16 to 47 (excluding batches 8 to 15, 21 and 41 which were apparently collected when cooling water was on), was 14,100 mg/l, somewhat lower than the 18,000 to 20,000 mg/l preliminary COD data. This is primarily important for determining the total load from the evaporator, should a design ultimately be developed based on these studies.

TABLE 7-1. FOUL CONDENSATE WASTEWATER CHARACTERISTICS PILOT PLANT DATA

Parameters	Raw Waste		Neutralized Influent (Batch 8 to 47) to Pilot Units[a]	
	Range	Average	Range	Average
pH	1.6 - 3.2	-	4.8 - 5.9	-
Temperature °C	95 - 100	98	30 - 40	35
Acidity mg/l	4700 - 11,500	7800	-	-
Alkalinity mg/l	-	-	2500 - 5800	4200
COD_T mg/l	8200 - 16,000	13,000	8300 - 16,000	13,000
BOD_T mg/l	-	-	6000 - 13,000	9900
Volatile Acids mg/l	6000 - 14,000	9100	5100 - 11,000	8400
Color PCU	15 - 250	32	15 - 800	170
TS mg/l	-	-	6300 - 13,000	11,000
TVS mg/l	-	-	1800 - 6200	3800
SS mg/l	-	-	9 - 220	44
VSS mg/l	-	-	4 - 114	28
PO_4 as P mg/l	-	-	3 - 59	40
TKN as N mg/l	-	-	64 - 820	210
NH_4 as N mg/l	-	-	56 - 260	150
$S^=$ as S mg/l	-	-	3 - 243	36
SO_3 as SO_3 mg/l	-	-	44 - 720	300
SO_4 as SO_4 mg/l	-	-	45 - 930	280

[a] Batches 1 to 8 supplemented with acetic acid to COD 15,000 mg/l.

The raw waste was prepared for feeding to the pilot units by neutralization and by the addition of the nutrient chemicals listed in Table 4-3. Lime and caustic were added in equal proportion for batches 1 to 17. Initially the waste was neutralized to pH 6.5 to 6.8, and both chemicals were used to avoid any possible inhibition due to cation concentrations. As the waste acclimated in the pilot units, neutralizing chemicals were reduced, and from batch 8 (day 45) to 47 the alkalinity and pH maintained in the influent waste were fairly constant, as can be observed on Figure 7-2. From batch 17 (day 74) to 47 (end of study) only caustic was used for neutralization due to scaling problems in the pilot plants. The average addition of caustic alkalinity was 5960 mg/l as $CaCO_3$. Influent volatile acids, COD, BOD, and TOC are also illustrated on Figure 7-2. Influent parameters analyzed are shown in Table 7-1. Nitrogen was added to the waste to ensure there was no deficiency. Initially, 150 mg/l of nitrogen was added to batch 1 to 8; nitrogen addition was decreased to about 45 mg/l for the remainder of the study. Study effluent data indicated that nitrogen addition probably was not required.

Twenty five to 30 mg/l phosphorus was added to all the raw waste batches to ensure phosphorus was not limiting to biological treatment. The effluent data indicated that lower amounts of phosphorus would probably have been adequate. Trace nutrients listed in Table 4-3, were added to the raw waste, starting with batch 4. Raw waste and influent analytical data are tabulated in Volume 2, Appendix.

Sludge Acclimation

Active digesting sludge was put into a reactor tank near the pilot plant area. The 2000 liter tank was insulated and equipped with a heating tape and recirculating pump. Anaerobic filter flexi rings were put into the tank along with the sludge. An acetic acid substrate of about 20 gm/l COD concentration was neutralized and fed to the sludge. Gradually, as shown in Table 7-2, foul condensate waste was added to the feed to the unit. The unit was fed on the basis of maintaining volatile acids in the recirculated reactor contents below approximately 1000 mg/l and the

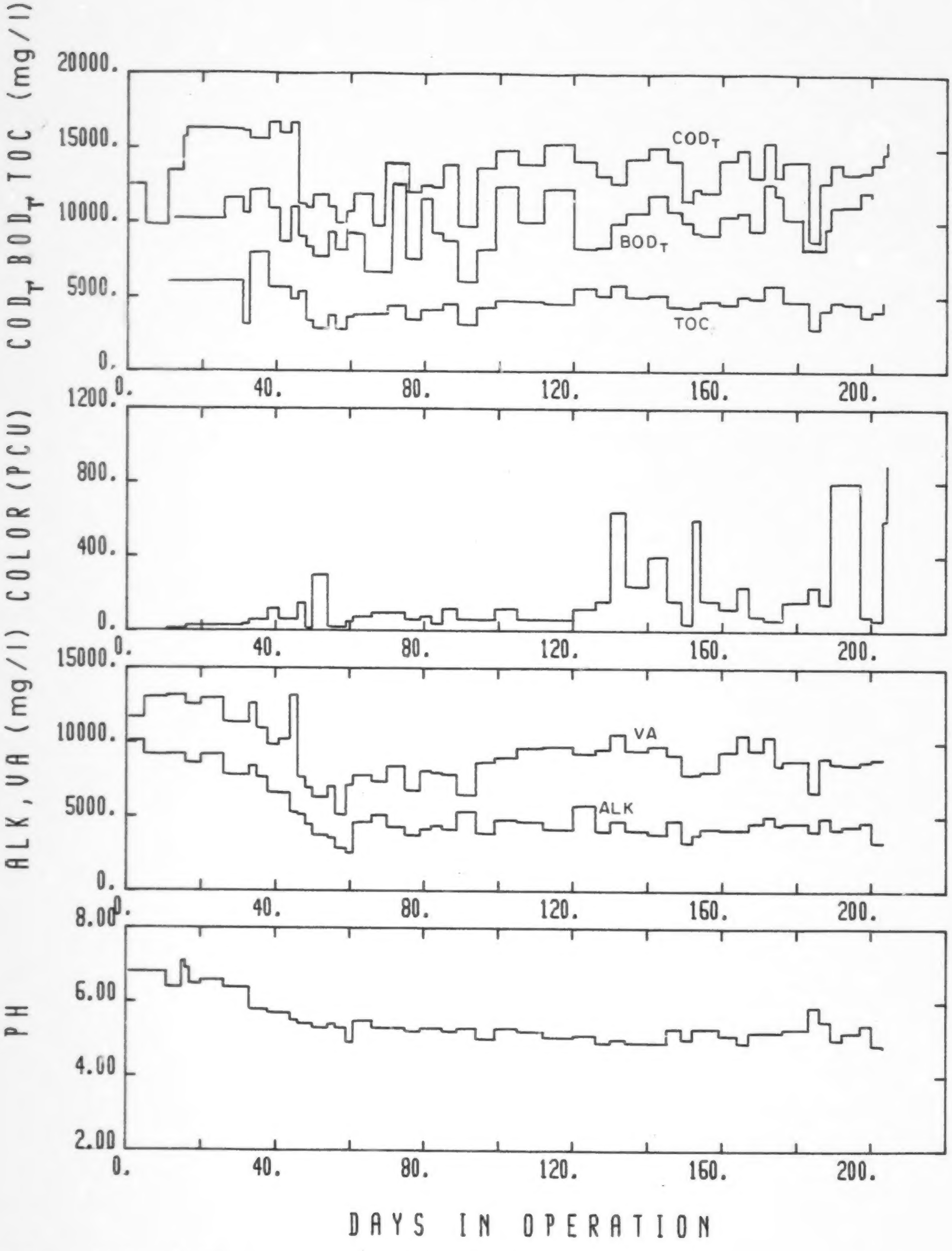


Figure 7-2. Influent waste characteristics.

observed gas production. As can be seen, the sludge did well on the acetic acid substrate; however, loadings had to be significantly reduced after the foul condensate was introduced during the third week. During the seventh and eighth weeks, the foul condensate was increased rapidly, and although the loading was quite low, gas production continued, indicating acclimation was apparently taking place. Procter and Gamble's special report on the acclimation program is included in Volume 2, Appendix.

TABLE 7-2. SLUDGE ACCLIMATION DATA SUMMARY

Week Number	Volume Fed (l)	Days Fed	Gas l/d[a]	Percent Condensate by Volume in Feed
1	61	1	ND	0
2	624	4	422	0
3	681	5	491	5-10
4	284	3	209	10
5	79	2	31	10
6	91	2	460 (3b)	10-20
7	183	4	101 (2b)	20-40
8	95	2	115 (3b)	40-70

[a] Gas production based on average production on days measured (0d).
[b] Days of measurement.

PILOT PLANT - STARTUP

The pilot plants were set up and were ready for seeding by January 7, 1983. The fluidized bed unit had been started up previously; however, excess caustic feed resulted in a pH of 12.1 in the reactor and the unit had to be reseeded. The settled acclimated sludge was transferred to the upflow bed and filter pilot units. The filter also received the slime coated media from the acclimation tank, as well as fresh media to fill the entire media zone in the reactor. The pilot units were then filled with an influent feed with a COD of 15 g/l, consisting of 20 percent neutralized foul condensate and 80 percent acetic acid substrate. The influent pH was adjusted to 6.8. All three units were operated on recycle with a small influent flow to compensate for evaporation and sampling losses. Due to high effluent solids from the upflow bed, the effluent was settled and solids recycled starting day 10.

Decreasing effluent volatile acid concentrations were measured on all three units as shown on Figure 7-3. An increase in gas production was also noted. Foul condensate was increased to 40 percent in batch 2, day 15; 60 percent in batch 3, day 25; and 100 percent in batch 4, day 33.

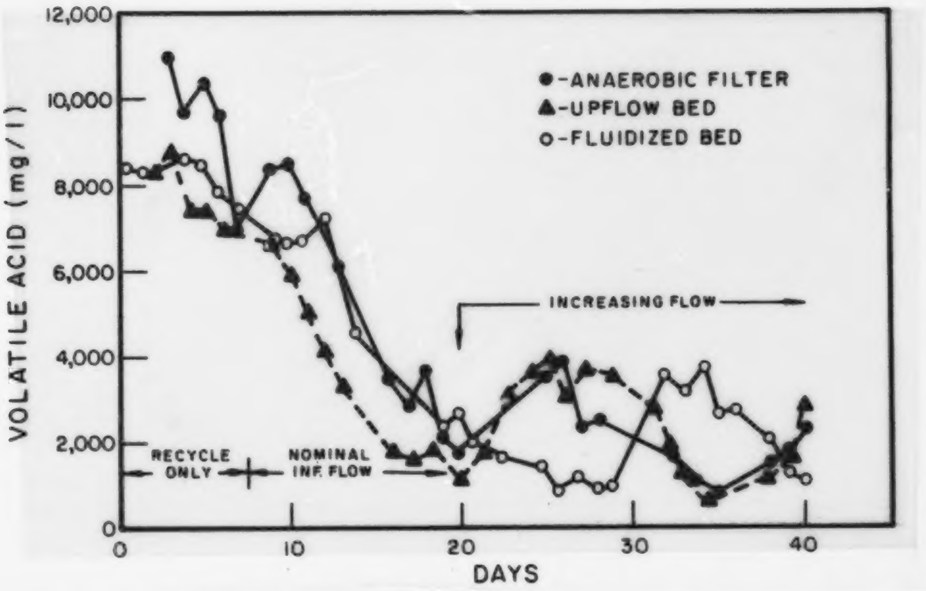


Figure 7-3. Pilot plants startup volatile acid concentrations.

From day 13, influent flow was gradually increased to the filter and upflow bed pilot plants. Based on volatile acid concentrations in the effluents, initial startup was considered achieved by day 21. COD loadings were then adjusted upward, during the next 20 days, based on effluent volatile acids concentration. By day 39, COD loadings on all three pilot plants exceeded 6 kg/m^3-d, with removals of 76 to 84 percent. Loadings of 6 to 7 kg/m^3-d were then maintained on the units for the first loading period, commencing with day 46. Operating and analytical data on the pilot units are tabulated in the Appendix.

PILOT PLANT LOADING PERIODS--COD LOADINGS AND REMOVALS

Chronological plots of key system parameters were developed for each of the pilot plants and provide an overview of the results of the study. The plots start on day 20, after the initial startup period, during which the units were primarily on recycle.

As previously described, the major objective of this study was to develop organic loadings and removals typical of results reviewed in the literature summary on the pilot systems, and to observe performance during at least two constant loading periods. It was recognized that the very slow growth and retention of methanogenic organisms, and the variable nature of the wastewater would probably preclude achieving a steady state situation. Based on observations of the data, and normal operating conditions as previously described in Section 6, it had been determined that a steady state period would be generally defined as a two week period during which loading, COD removal, and gas production were judged to be fairly constant. COD removal was based on the COD of the total influent sample and COD of the filtered effluent samples.

To more clearly illustrate the chronology of the pilot unit results, COD loading and percent removal data were averaged over periods of consecutive days. Some of the periods were at a steady state, as defined above; however, other periods were quite variable in loading or operation. The plots for each of the pilot plants illustrate average conditions and the loading periods analyzed. Data collected during the selected loading periods are representative of constant conditions of loading and removal and are presented in tabular form, with a discussion on each pilot plant. The COD removal was based on the COD of the total influent sample and COD of filtered effluent samples.

Anaerobic Filter

Figure 7-4 illustrates the chronological results of the operation of the anaerobic filter. Figure 7-5 presents the averaged COD loadings and

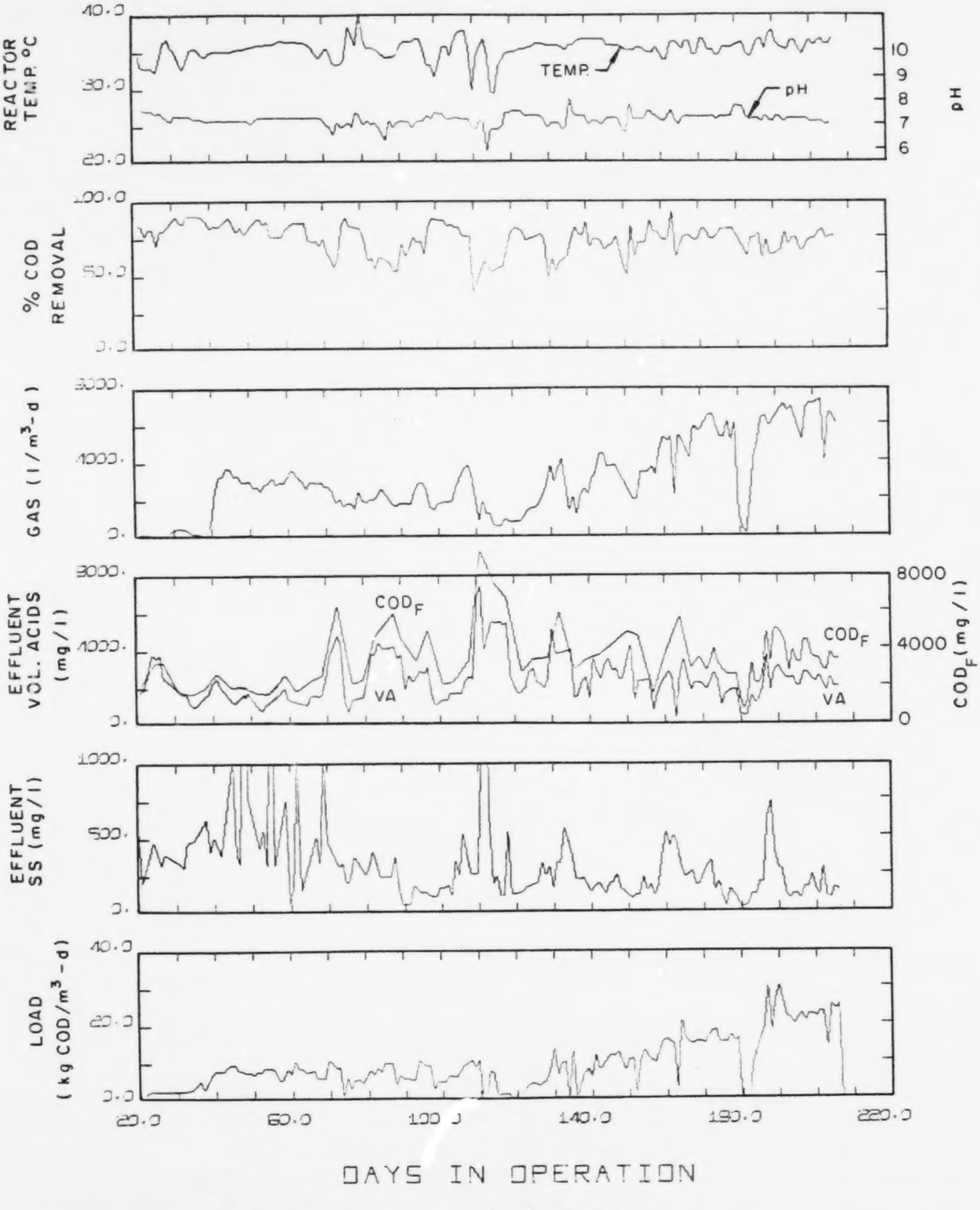


Figure 7-4. Anaerobic filter chronological data.

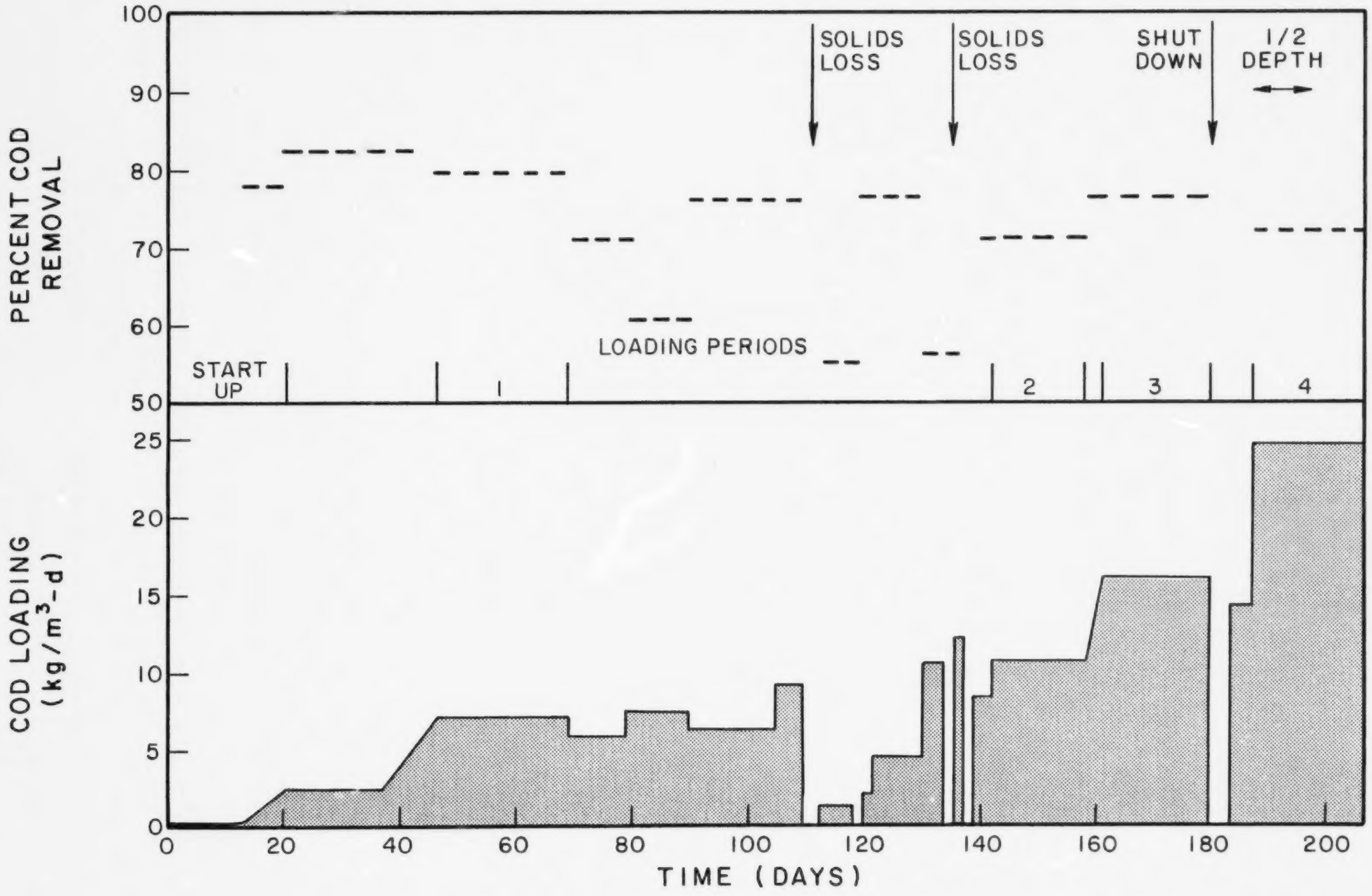


Figure 7-5. Averaged COD loading and removal efficiency-anaerobic filter.

removals for successive periods during the pilot study. Also shown on the Figure are the three periods of relatively constant loading and removal and a fourth special study period. Between these periods, the pilot plant operation or results were variable due to either upset problems or intentional load variation to develop increased removal capacity. The data during the constant loading periods were averaged, and are presented in Table 7-3.

On day 45, the first constant loading was started at a planned operating loading of approximately 7 kg COD/m^3-d. As can be seen in the chronological plot, effluent volatile acids, COD concentrations, and COD removal varied within a reasonably narrow range up to day 70. Loading then increased from 5.5 to over 10 kg COD/m^3-d due to a change in influent concentration and flow rate, and resulted in increased volatile acids and depressed pH. Up to this time, loading to the unit was fairly constant; except for several days at low loadings and a slight overload on one day. Effluent suspended solids were very variable. This was attributed to washout of the seed sludge and sampling problems experienced due to clogging of the sample pump lines. This problem was corrected by use of a different type sample pump (peristaltic) starting on day 55. During this first period, a number of operational problems occurred. Due to the dilution of the condensate at the evaporator, the waste COD concentration varied, thus to maintain a constant load, the flow had to be varied. This was corrected in subsequent periods as previously described. Occasional deviations of flow rate from that set with the controllers occurred, due to the varying level in the storage tanks and use of a bypass around the influent feed pump for flow control. Closing the bypass eliminated this problem. Flow and temperature control problems were experienced due to line and heater fouling with scale due to neutralization of the waste with lime. Accordingly, only caustic was used to neutralize the waste starting on day 77, and after cleaning out the lines and heater, no scaling problems were experienced in subsequent periods. Data was analyzed for the first period through day 69, prior to the overload and subsequent drop in removal efficiency on day 70, and are shown in Table 7-3.

TABLE 7-3. ANAEROBIC FILTER AVERAGE DATA FOR LOADING PERIODS

	Period (days)			
	46-69	143-158	164-179	187-207[a]
Loading COD				
kg/m^3-d	7.2	11.1	16.5	24.8
Detention d	1.5	1.1	0.9	0.6
Percent COD Removal[d]	80	69	77	72
Percent BOD Removal[d]	83	72	78	77
Percent TOC Removal[d]	83	66	80	87
Gas				
m^3/kg COD_R	0.51	0.46	0.45	0.44[b]
Percent CH_4	74	69	68	66
m^3/m^3-d[c]	3.0	3.6	5.6	7.9
Influent mg/1				
COD_T	10,600	12,400	14,000	13,900
BOD_T	8,400	9,900	11,000	11,500
TOC_T	3,670	4,180	5,160	8,760
VOA	6,910	8,460	9,540	8,760
SS	21	46	29	76
Total S	210	370	270	194
Effluent mg/1				
COD_F	2,090	3,860	3,280	3,840
BOD_F	1,420	2,780	2,370	2,680
TOC_F	640	1,400	1,020	1,110
VOA	1,290	2,630	2,150	2,450
SS	680	162	199	228
Total S	130	325	211	197

[a] Includes one half depth study period 187-196.
[b] See Section 8 for discussion of gas measurements data day 187-207.
[c] Cubic meters of gas generated per cubic meter of reactor volume.
[d] Percent removals based on total influent, filtered effluent.

During this period, average effluent solids were quite high, and varied from 50 mg/l to over 2000 mg/l. The COD removals fluctuated from 68 to 88 percent, however, they were generally in the range of 80 to 85 percent. Effluent volatile acids varied from 700 to 1900 mg/l and were typically in the range of 1000 to 1500 mg/l. The variations in effluent COD and volatile acid concentration were related to the variations in loading. The loss of solids apparently resulted in a decrease in the removal capacity of the filter toward the end of the period as indicated by increasing effluent volatile acid concentration at slightly lower, 5 to 6 kg COD/m^3-d, loadings.

Loading was reduced about one-third on day 78 to 79 and then gradually brought back up. Temperature control problems occurred around day 83 and poor removals were measured. The system was recovering, and loadings of 10 kg/m^3-d were being imposed, when on day 110, the bottom connection on the pilot unit broke, draining the unit. Approximately two weeks at lower loadings of 2 to 5 kg/m^3-d were required to bring the effluent volatile acids down to previous levels. Loadings were gradually being increased to 10 kg/m^3-d, when on day 134, a line burst, partially draining the unit. Recovery from this occurrence was fairly quick. After about one week, day 141, loadings had been increased to the second loading range of about 10 to 12 kg/m^3-d. Volatile acid concentration and COD removals were similar to those achieved around day 106, prior to the problems.

During the subsequent period, heavy foaming occurred in the pilot unit clogging the gas meter for several days. Reduction of flow rate did not reduce foaming. The foam spray system was put into operation and controlled the foam, which unexplainably decreased markedly by day 158. A review of data during day 143 to 158 (despite the problems encountered), indicated a fairly constant loading except for two days of low loading, and fairly uniform removals except for those two days. The average results during day 143 to 158 were analyzed, and are shown in Table 7-3. Conditions were not constant, because of the foaming and variable loading; and therefore, removals were lower than expected.

The loading to the filter was increased to about 15 kg/m^3-d on day 159, and the unit generally operated at loadings in the range of 15 to 20 kg/m^3-d until the plant's July 4 shutdown, day 180. During this period, the foam spray was augmented with an additional spray nozzle and no problems due to foaming occurred. No waste was available on day 163 and the unit was over fed on day 164. Operations were reasonably constant and normal during the the third loading period, except for these two occurrences. Average data from day 164 to 179, are shown in Table 7-3.

The average loading was 16.5 kg/m^3-d and the average COD removal was 77 percent, ranging from 61 to 83 percent. Following the plant shutdown, the pilot plant loading was increased to 34 kg/m^3-d; however, volatile acids increased to over 3000 mg/l, and the loading was reduced to 20 to 25 kg/m^3-d until the end of the study.

A half depth loading study on the lower section of the filter was conducted during this period and the results are presented and discussed in Section 8. The data during the period, at one-half depth and full depth, but at a similar volumetric loadings were combined and are shown in Table 7-3. The data showed the progressive development of the filter's removal capacity, since percent removals at the higher loading of 25 kg/m^3-d were only slightly lower than those achieved during the previous period at a lower loading of 16.5 kg/m^3-d. This concluded the anaerobic filter pilot plant study.

Upflow Bed

Figure 7-6 presents the chronological results of the operation of the upflow sludge blanket bed. Maximum loadings to this unit were achieved relatively early in the study during the first loading period. Figure 7-7 presents the averaged COD loadings and removals for successive periods during the study. Similar to the anaerobic filter, relatively constant loading and operation periods are indicated. A rather long period of poor operation and upset was experienced between loading periods one and two. The data from the loading periods were averaged and are presented in Table 7-4.

Problems in maintaining flows and clogging due to scale were also experienced with the upflow bed unit during the initial loading period, starting with day 46. Loading to the unit was maintained in the same range up to day 69 except for several days of low loadings in the middle of the period, and at the end of the period. As shown in the chronological plot variations in parameters during the first period in the upflow bed were somewhat greater than in the filter. Temperature problems were more

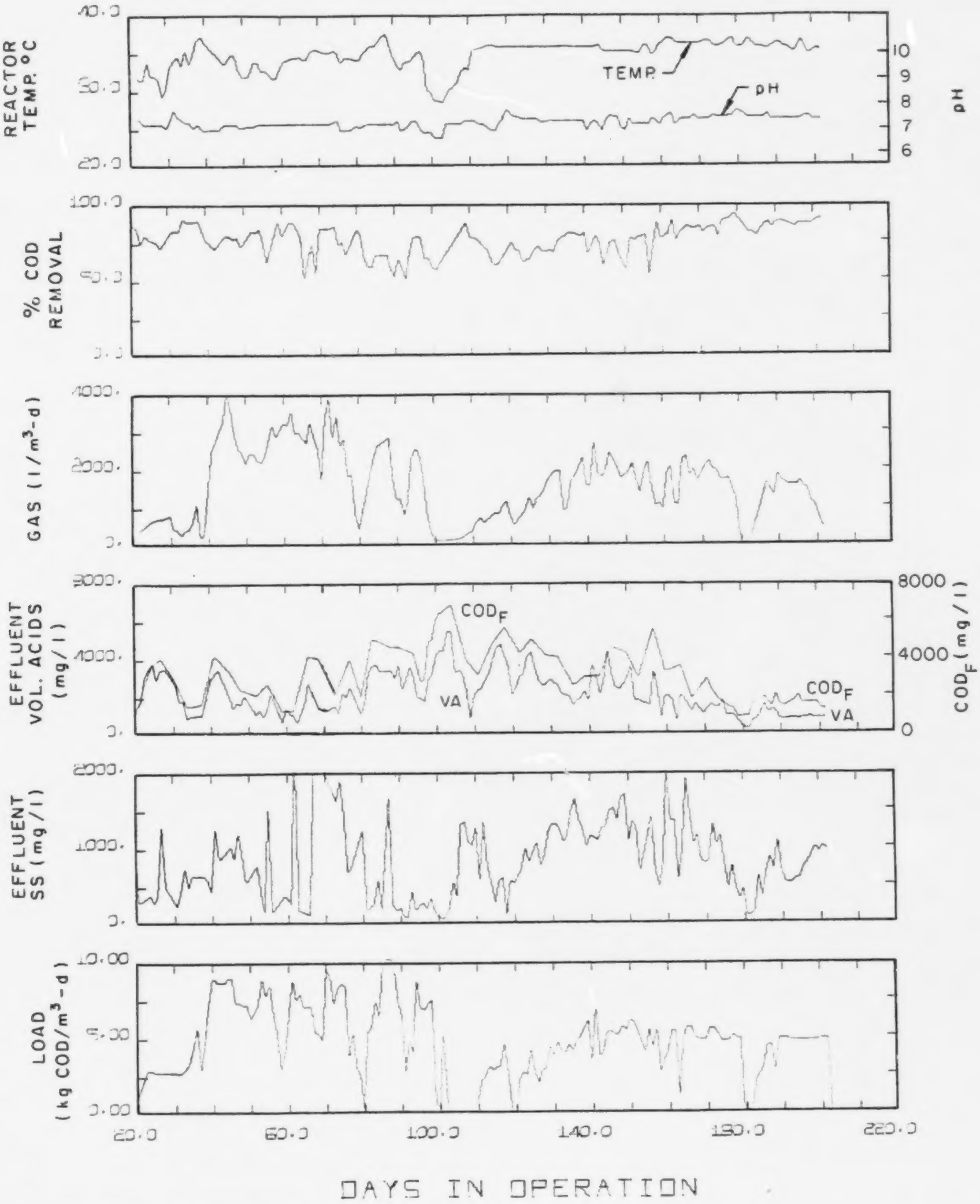


Figure 7-6. Upflow bed chronological data.

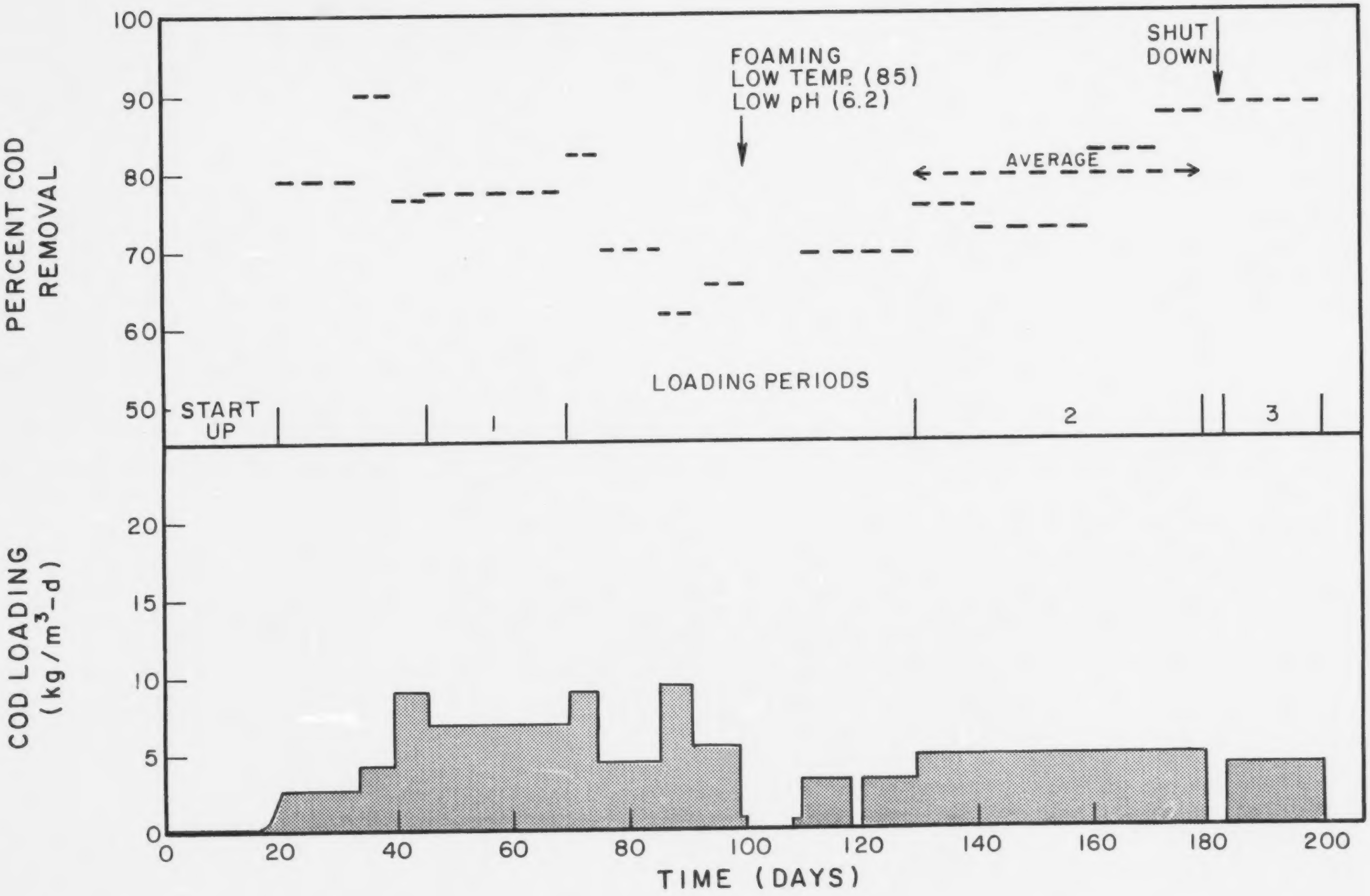


Figure 7-7. Averaged COD loading and removal efficiency-upflow bed.

severe, and loading fluctuations greater, resulting in greater variations in effluent COD and volatile acids concentrations.

TABLE 7-4. UPFLOW BED AVERAGE DATA FOR LOADING PERIODS

	Period (days)		
	46-69	129-179	183-202
Loading COD			
kg/m^3-d	6.7	4.9	4.4
Detention d	1.6	2.3	2.9
Percent COD Removal[a]	76	79	87
Percent BOD Removal[a]	83	79	89
Percent TOC Removal[a]	79	81	92
Gas			
$m^3/kg\ COD_R$	0.52	0.48	0.40[b]
Percent CH_4	74	68	72
m^3/m^3-d	2.8	1.8	1.6
Influent mg/l			
COD_T	10,600	13,600	12,700
BOD_T	8,400	10,600	10,700
TOC_T	3,670	4,930	4,010
VOA	6,910	9,210	8,420
SS	21	33	70
Total S	210	267	196
Effluent mg/l			
COD_F	2,520	2,860	1,680
BOD_F	1,450	2,190	1,210
TOC_F	780	940	310
VOA	1,440	2,000	960
SS	1,090	1,150	730
Total S	109	209	175

[a] Removal based on total influent-filtered effluent.
[b] Gas data day 185 to 199.

During the later part of this period, the effluent clarifier used during startup to recycle settleable solids was removed from operation, and the unit was operated in the sludge bed mode. Effluent solids were generally quite high and were lost from the system. Averaged data during the first loading period, were over the same period as both the filter and fluidized bed.

Although the clarifier was returned to use on day 84, apparently the loss of solids, low temperature periods, and foaming, all contributed to a significant loss in removal capacity by day 100, when volatile acids increased to over 5000 mg/l. Loadings from day 100 to 125 were reduced to 0 to 3 kg/m^3-d to reduce the volatile acids concentrations. Based on effluent volatile acid concentrations and gradual buildup of removal capacity, loadings were increased to approximately 4 to 6 kg/m^3-d by day 129. Fairly uniform loadings were imposed on the unit from about day 129 to 206, during which period COD removal efficiency gradually increased from 75 to 85 to 90 percent, as can be seen on Figure 7-7. Effluent solids were generally quite high, often 1000 mg/l or more, and it was necessary to utilize the external clarifier to settle and return solids to the system. A rapid settling pelletized type sludge was reported to be developed in this type system on certain other wastes,(1) but it did not develop during this study.

As shown on Figure 7-7, COD removal was above 70 percent during the first loading period. COD removal decreased and fluctuated from 50 to 70 percent during the following variable state period. Toward the end of the study, at a constant loading of 4 to 5 kg/m^3-d, the COD removal was in the 80 to 90 percent range. Table 7-4 presents data during the initial loading period, and for two periods of similar loading and operation. Although the loading during the two periods was similar, the data were divided to show the higher percent COD removals being attained in the latter period, illustrating the gradual buildup of removal capacity in the unit. A decrease in unit gas production during the last period was observed. During the final four days of data, the gas production appeared to be abnormally low based on previous data and COD removals. The reason for the low gas measurement was not determined. Based on the removal capacity being achieved at the end of the study, the unit probably could have been subsequently loaded at 5 to 7 kg/m^3-d and achieved removals of 70 to 80 percent, similar to the removal level being obtained by the filter at a loading of 20 to 25 kg/m^3-d.

Fluidized Bed

The chronological plot of the fluidized bed data is shown on Figure 7-8. Figure 7-9 presents the averaged COD loadings and removals for successive periods during the pilot study. Similar to the other two units, loading periods are indicated. Figure 7-9, however, has a scale on the COD loading four times that on Figures 7-5 and 7-7. One variable loading period and two upset periods were experienced with the fluidized bed pilot plant. Loading periods toward the end of the study were somewhat short; however, data indicated fairly constant removals were being achieved. The loadings to the pilot unit had been increased after short periods in an attempt to push the pilot plant to its limit. Longer operation at these loadings may have resulted in some increase in removal, assuming additional solids would be accumulated in the bed. These abbreviated periods, therefore, may not be representative of "equilibrium" conditions, although loading and removals were fairly constant. High removals, however, were achieved at loading rates significantly greater than had been reported in the literature reviewed in Section 3. Data presented in Table 7-5, from each period, were averaged separately to illustrate results obtained under the operating conditions during that period.

During the initial loading period, day 46 to 69, the initial loading rate to the fluidized bed was held constant in order to compare with the other two units. The effluent solids from the fluidized bed unit were quite high, until about day 55, after which they decreased significantly. As mentioned previously, the effluent sample pumps had been replaced with a finger pump on day 55 due to continual excessive clogging of the pump valves due to high suspended solids. Whether this had an effect on the fluidized bed effluent solids cannot be concluded from the data.

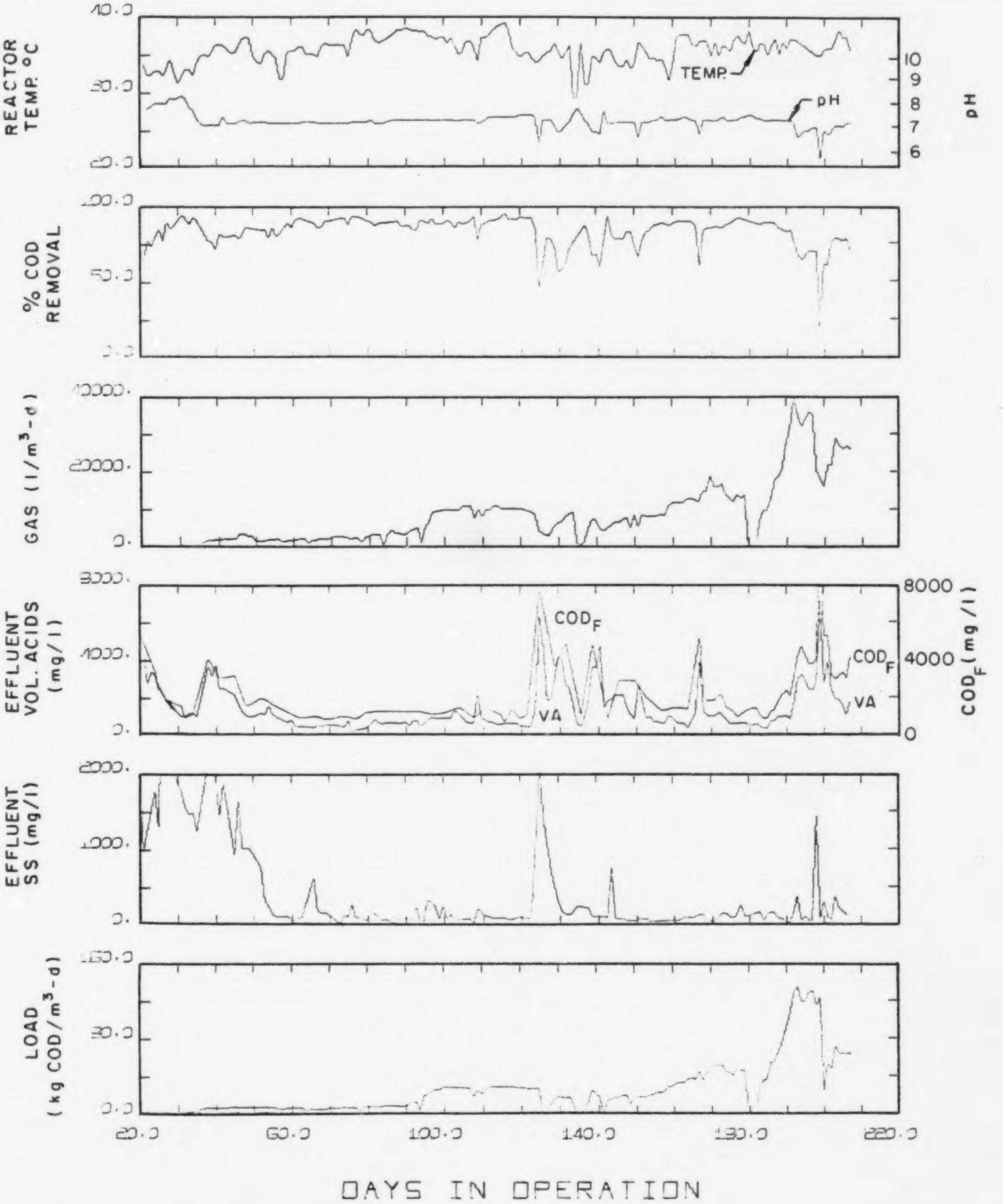


Figure 7-8. Fluidized bed chronological data.

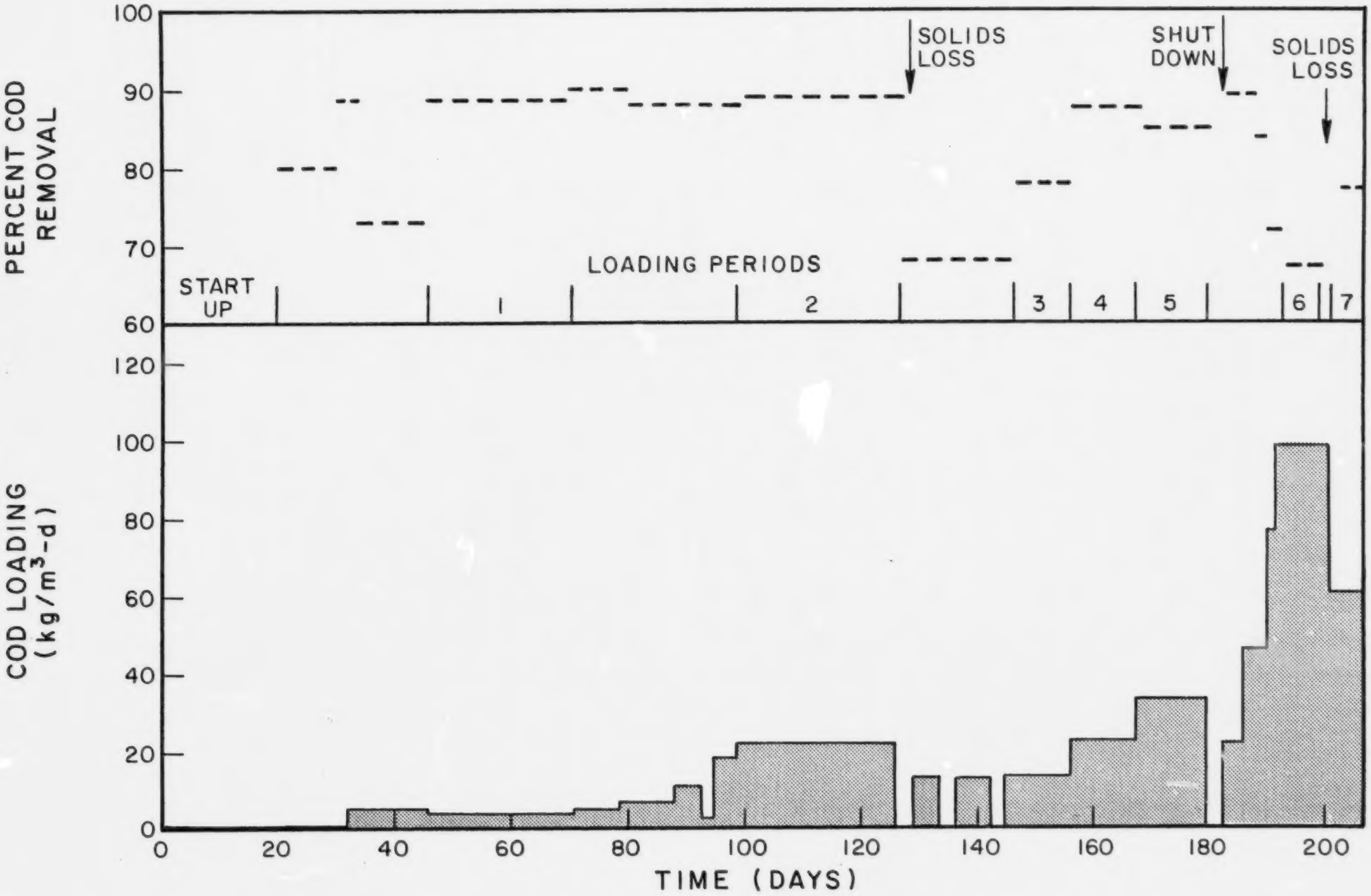


Figure 7-9. Averaged COD loading and removal efficiency-fluidized bed.

TABLE 7-5. FLUIDIZED BED AVERAGE DATA FOR LOADING PERIODS

Period	46-69	97-124	145-155	156-166	168-179	193-198	202-207[a]
Loading COD							
kg/m^3-d	6.1	24	17	25	35	102	64
Detention d	1.7	0.52	0.64	0.42	0.29	0.10	0.2
Percent COD Removal[b]	88	92	79	90	86	69	78
Percent BOD Removal[b]	91	93	81	93	83	68	-
Percent TOC Removal[b]	91	96	80	93	87	-	-
Gas							
$m^3/kg\ COD_R$	0.44	0.48	0.54	0.51	0.50	0.46	0.54
Percent CH_4	71	69	65	71	69	62	64
m^3/m^3-d	2.4	10.2	7.4	11.6	15.0	32.3	26.8
Influent mg/l							
COD_T	10,600	14,500	12,400	14,600	13,900	13,300	15,500
BOD_T	8,400	10,800	9,900	10,600	11,100	11,400	-
TOC_T	3,670	4,930	4,480	4,840	5,170	4,270	-
VOA_T	6,910	9,410	8,220	9,970	9,290	8,600	-
SS	21	73	46	30	29	106	142
Total S	210	173	370	222	278	190	203
Effluent mg/l							
COD_F	1,290	1,150	2,620	1,400	1,900	4,180	3,330
BOD_F	760	740	1,900	710	1,840	3,650	-
TOC_F	320	214	920	330	650	-	-
VOA_F	840	820	1,540	750	1,120	2,390	1,800
SS	420	140	62	75	124	147	200
Total S	233	162	355	220	227	136	134

[a] Simulated 24 hour composite waste, COD data only.
[b] Removal based on total influent-filtered effluent.

Following the first period, loadings to the fluidized bed were gradually increased until day 96 when a second loading period was started. This period lasted until a power outage occurred on day 124, which seriously disrupted the unit. A significant solids loss from the bed occurred, indicated by a 17 percent decrease in bed volume. Loadings had to be decreased in order to restore previous effluent volatile acids concentrations. A second power outage occurred on day 134, further disrupting the unit's operation.

Loading was decreased over the next 10 days, 145 to 155 and average data during this recovery period is shown in Table 7-5. The loading was subsequently brought back to former levels and by day 160, the bed volume had increased to its former value. Effluent volatile acids and COD concentrations decreased, and removals increased to the 90 percent range. It was found possible to increase loadings over relatively short periods during which the unit responded quickly by establishing fairly constant removal levels. The unit was run at two average loading ranges for about 10 days each, 156 to 166 and 168 to 179. Removals remained high as shown in Table 7-5. The unit was put on recycle only, for the plant's July 4 shutdown (day 180).

Temperature control was somewhat more variable with this small pilot unit than with the two larger pilot plants; however, temperatures were generally within three degrees of the 35°C goal with one, two day exception during which temperature decreased to 29°C. The system usually operated at a pH of 7.0 to 7.4; however, as loadings were increased, and before additional solids built up in the reactor, decreases in pH to 6.5 to 7.0 over one to two days were experienced, with no apparent difficulties.

After the plant shutdown and no feed to the unit for three days, loadings were increased to the unit as rapidly as possible, from day 183 to 192. Effluent volatile acids concentrations increased, and percent COD removal decreased; however, exceptionally high loading and removal rates were rapidly attained. The exceptionally high loading rate period ended when a large solids loss in the bed occurred on day 198. The loss was attributed to the high gasification rate which resulted in gas being trapped in the recycle stream and causing solids stripping from the media. The bed volume decreased 26 percent due to solids loss; however, after three days the unit was performing quite well at a reduced loading, and the bed was rapidly increasing.

Since the periods were short, they may not be considered as steady state results by previous definition, although fairly constant removals were being achieved. During the five days the loading to the unit was in the range of 94 to 111 kg COD/m^3-d, the detention time of the waste in the reactor was less than five hours, thus there were theoretically about 25 displacements of the pilot plant volume during this time. The removals achieved under these conditions are shown based on five daily composite samples. Although the system may not have been run long enough to achieve a constant steady state removal capacity, the results indicate that the removal capacity demonstrated by the data was exceptionally high compared to previously reported data reviewed in Section 3. There was no reason to expect that removals at these high volumetric loadings would decrease as long as the biological solids were retained in the system. This was indicated by the ratio of COD loading to volatile solids in the unit determined at the end of the study and discussed in Section 8. Potentially, with further growth and development of the sludge bed, greater removals may have been possible at these loadings. An analysis of the kinetics in the fluidized bed is presented in Section 8.

Summary

During this six month pilot study, all three anaerobic systems demonstrated the anaerobic treatability of the foul condensate wastewater. Despite a number of operational problems during the middle parts of the study, the anaerobic filter demonstrated reasonably good COD removals, 70 to 80 percent, at volumetric loadings of up to 20 to 25 kg/m^3-d by the end of the study. With the further development and buildup of removal capacity which seemed to be occurring toward the end of the study, higher removals and/or loadings may have been achieved. The loadings and reasonable removals which were achieved were significantly higher than the design level of 10 kg/m^3-d used for full scale anaerobic filters.$^{(2)}$

The upflow bed unit also experienced operational and functional (solids too low) problems, and although high percent COD removals were achieved, loadings were relatively low compared to the filter and fluidized bed. An external clarifier was required to settle and return solids to the reactor to maintain and buildup removal capacity; however, the increase in capacity was quite slow at the loading of 4 to 5 kg/m^3-d. A hoped for, highly settleable sludge was not developed in the reactor during this study. Examination of solids in the reactor at the end of the study, however, did indicate a residual concentrated sludge of 3.2 percent volatile solids in the bottom 5 percent of the unit. If this sludge was not a residual seed sludge, but an accumulation of highly settleable solids, it would indicate that with time this sludge layer might have expanded and the unit could potentially have developed a greater COD removal capacity. The loading achieved with the upflow bed, including an external reactor, was in the range of 5 kg/m^3-d with removals in the range of 85 to 92 percent. This was typical of the design range for anaerobic sludge contact systems,(3) but lower than the 10-15 kg/m^3-d design range suggested for upflow sludge blanket systems.(4)

The fluidized bed unit demonstrated a significantly greater ability to develop COD removal capacity over relatively short periods of time than either of the other two units. This was clearly shown in the rapid increase in removal capacity from 8 to 10, up to 20 to 25 kg/m^3-d in about 7 to 10 days during the middle of the study. The rapid increase in removal capacity from 30 to 40 kg/m^3-d up to 70 to 80 kg/m^3-d within three to four days at the end of the study, was due in part to the removal of the lightly coated media from the bottom of the unit as well as an increase in unit capacity. These high removal rates had not been experienced previously and greatly exceeded the current conservative design loadings for the fluidized bed of 12 to 16 kg/m^3-day.(5,6) Based on solids measurements and data collected in this study, a simplified analysis of the kinetics of anaerobic treatment with the fluidized bed reactor was developed and is presented in Section 8.

Figure 7-10 shows percent COD removal as a function of volumetric COD loading for the various loading periods in the study, for each of the pilot plants. The loading was based on empty reactor volume. The variability within a loading period, particularly the low removals as previously discussed, was due in part to variable loadings rather than typical variation at a steady state condition. Some of the variability was due to slow development of removal capacity in the reactor as observed on the upflow bed and filter. Once the sludge bed was developed, the fluidized bed generally was able to readily adapt to a new loading in a fairly short time. Percent COD removal was fairly constant, over 85 percent, in the fluidized bed over the range of loadings up to 35 kg/m^3-d, and tapered off at the higher loadings up to 100 kg/m^3-d. These loadings were only run for a few days each, and it is conceivable that greater retention of biomass in

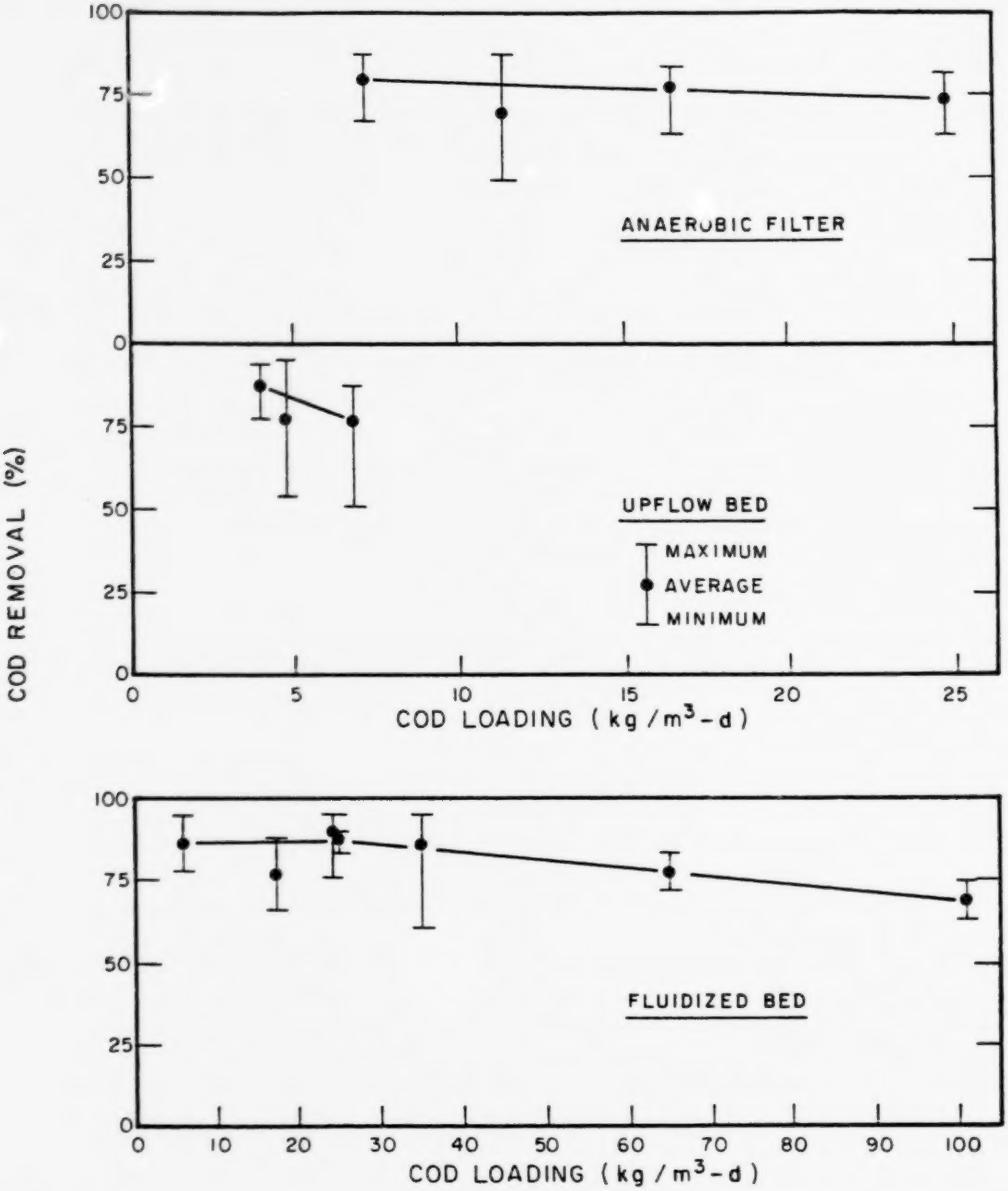


Figure 7-10. Loading period data, percent COD removal versus loading (volumetric basis).

the reactor may, with time, have resulted in greater percent removals. The filter also showed only a slight decline in removal up to the loading of 25 kg/m^3-d attained by the end of the study. In the upflow bed at lower loadings, high percent removal were achieved toward the end of the study, when COD removal increased from 80 to 90 percent.

Assuming an average design COD removal of 75 percent, design loadings based on this study would be: filter: 15 to 20 kg/m^3-d; upflow bed: 6 to 8 kg/m^3-d. A conservative value of 20 to 25 kg/m^3-d was considered at this time for the fluidized bed design, even though higher loadings appear possible, based on the short pilot plant operational periods at higher loadings and minimal full scale experience with operation of the anaerobic fluidized bed system.

SECTION 8

SPECIAL STUDIES--ADDITIONAL DATA ANALYSES

INTRODUCTION

Special studies were conducted during the course of the pilot plant study. These included tracer studies, tap sampling, and final solids profiles in the reactors. A half depth study and operation of the anaerobic filter with no recycle were conducted. The fluidized bed was operated on a simulated, equalized spent evaporator condensate which was characterized. Analyses of data collected during the study, in addition to volumetric loading and removals previously presented, included various data correlations, pH effect on gas composition, pH-bicarbonate alkalinity relationship, sulfur removal, calculated hydrogen sulfide content in the off gas, gas production correlation with COD removal and a calculated solids yield, effluent solids removal by clarification, a sieve analysis of the sand media in the fluidized bed, and a simplified kinetic analysis of the fluidized bed reactor.

TRACER STUDIES

Tracer studies were run on the three pilot units and the results are shown on Figures 8-1 and 8-2. A tracer, lithium chloride was added to the influent and effluent samples were collected and analyzed for lithium. The curves through the data points are representative of a theoretical completely mixed tank. Except for the upflow blanket test on March 31, these curves match the data quite well, indicating all three reactors were essentially completely mixed (very little to no plug flow). Mixing in the

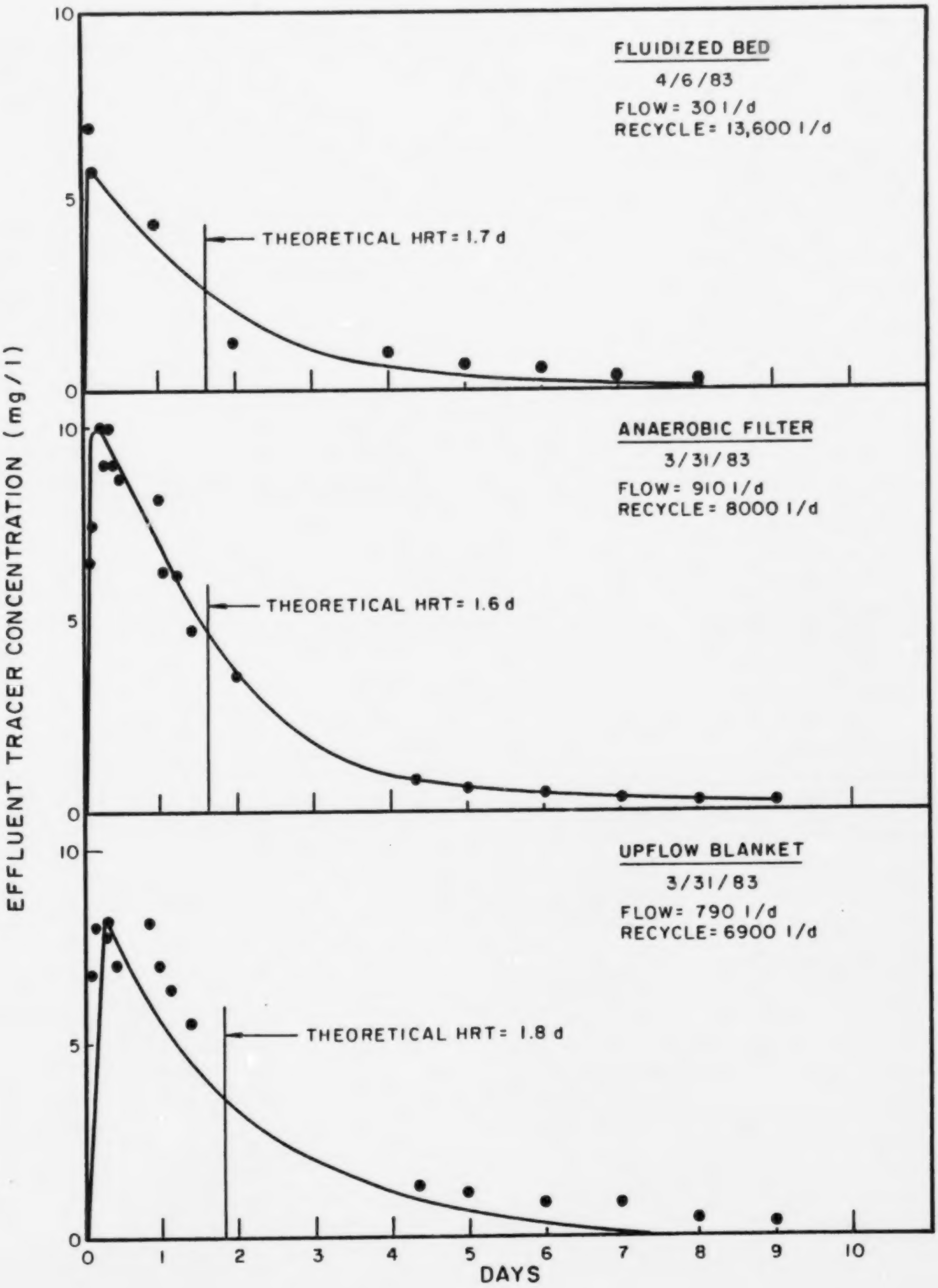


Figure 8-1. Lithium tracer study--days 83 and 89.

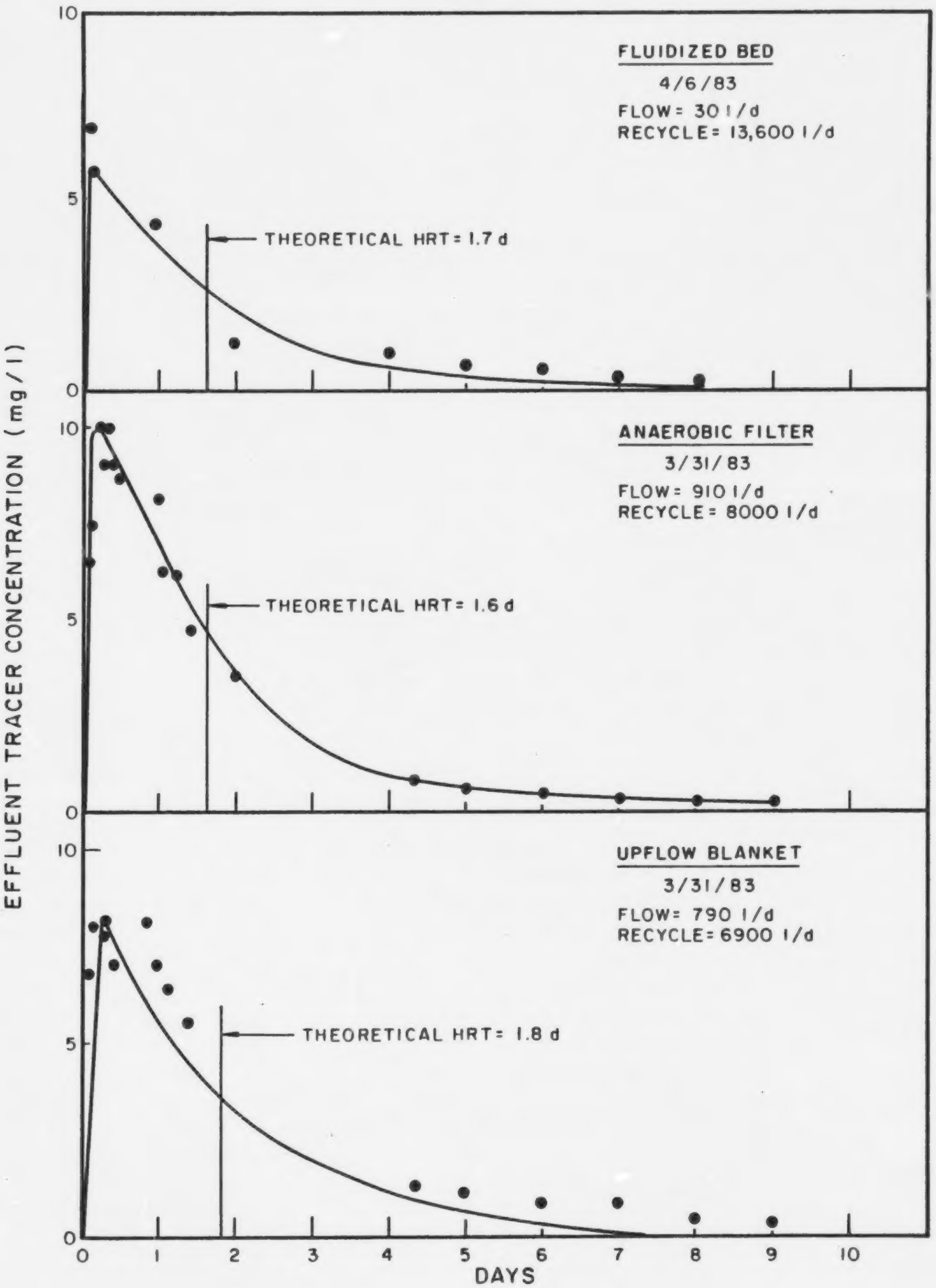


Figure 8-1. Lithium tracer study--days 83 and 89.

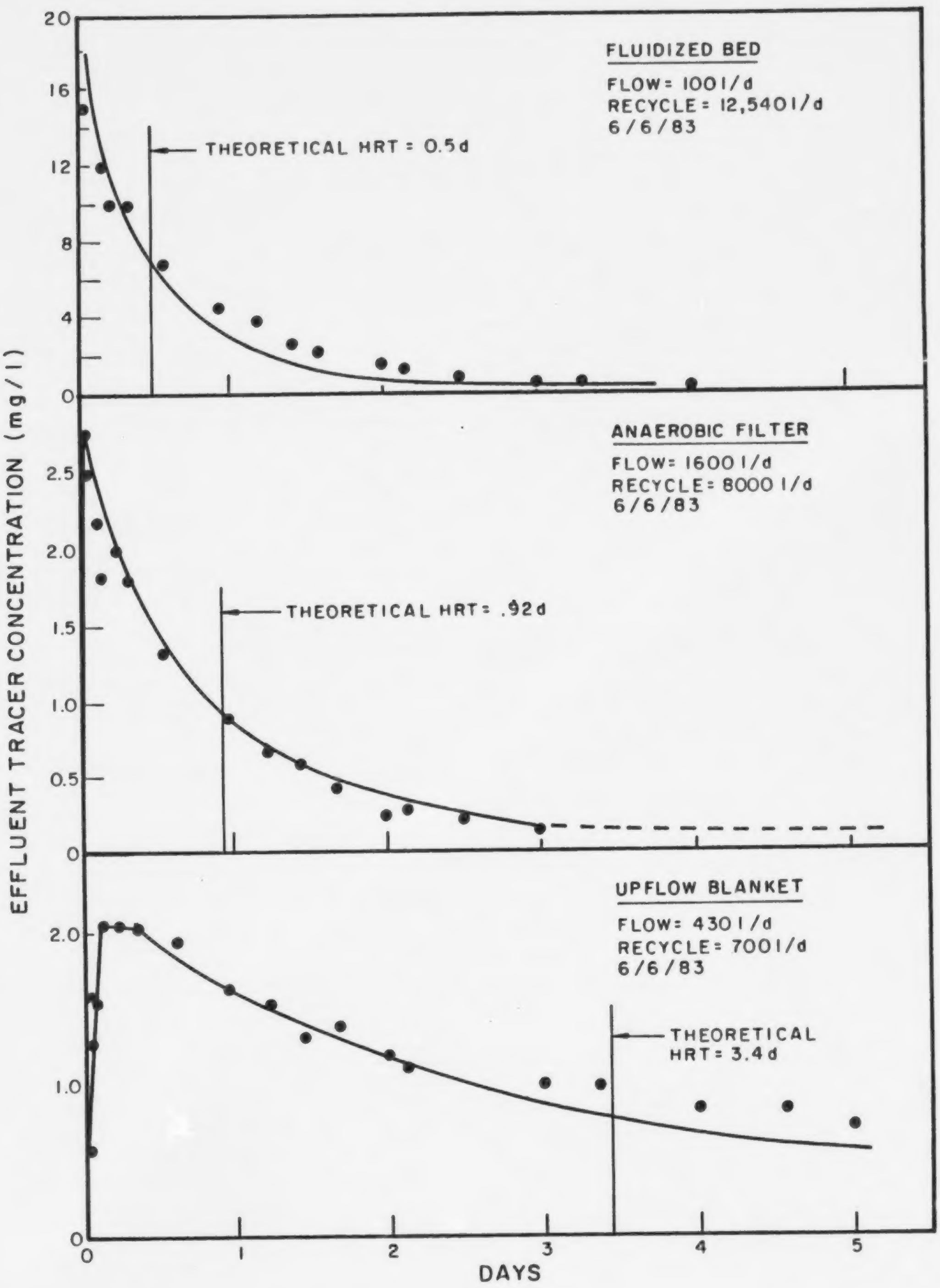


Figure 8-2. Lithium tracer study--day 150.

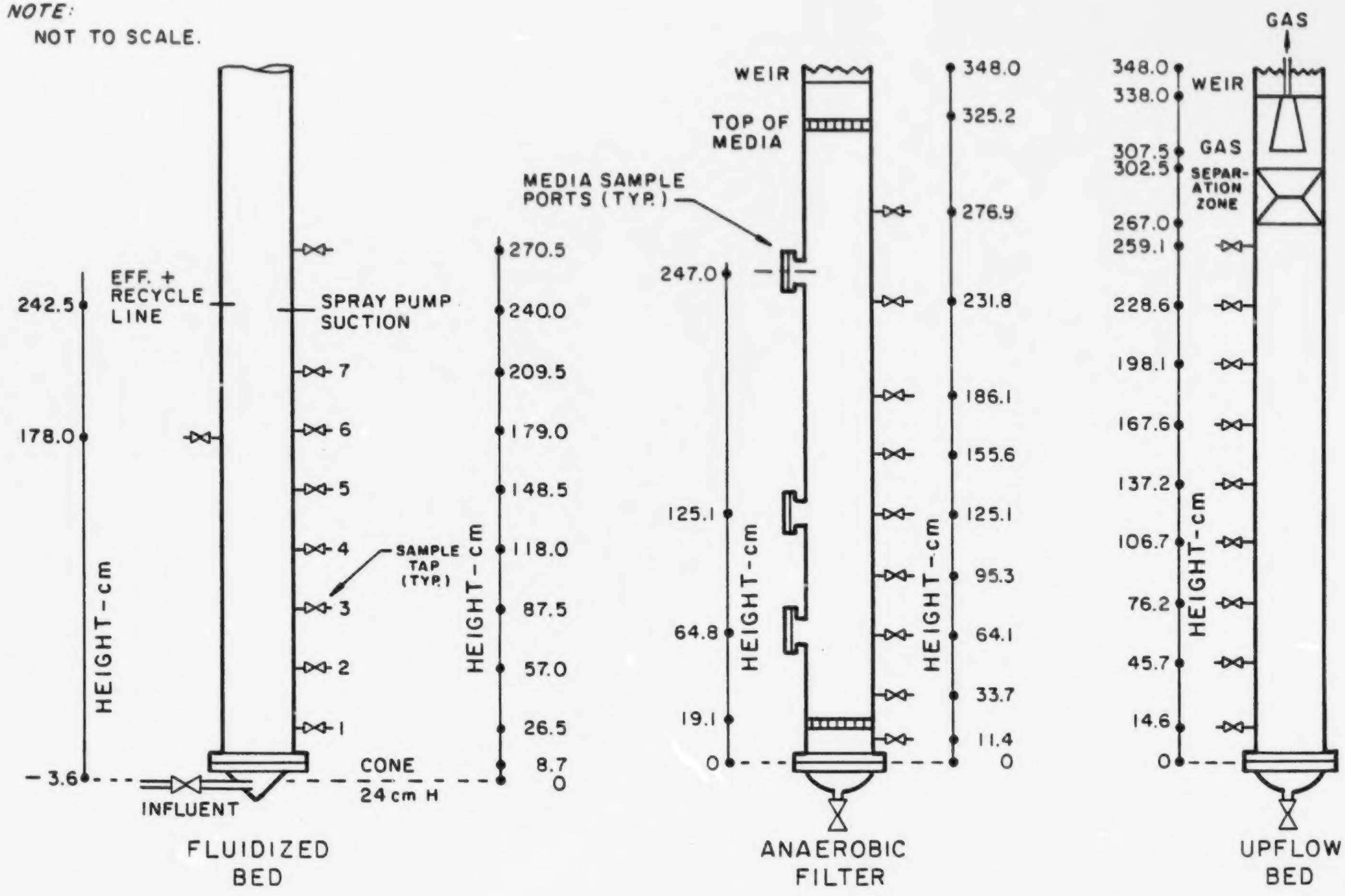
reactor was due to both the recycling of effluent and gas evolution in the anaerobic process. Theoretical detention times in the units were calculated based on a total liquid volume in the pilot plant and the influent flow rates. The total volume in the filter pilot plant based on 97 percent media porosity was 1500 liters, in the upflow bed 1460 liters, and in the fluidized bed 52 liters.

SAMPLING WITH DEPTH IN REACTORS

Figure 8-3 shows the location of the sample taps on each of the pilot plants. Several times during the study, the taps were used to collect samples at various depths to determine suspended solids concentrations and organic (or COD) removals. At the end of the study, each unit was sampled with depth as described in a subsequent section.

Data on volatile suspended solids in the filter and upflow bed units are shown on Figure 8-4. The initial sludge seed of up to three percent solids gradually washed out of both the filter and upflow bed. Table 8-1 shows the total suspended and volatile suspended solids in both units based on the measurements at each tap. Initially, the solids were 60 to 67 percent volatile; however, volatile solids decreased, probably due to the buildup of the calcium scale. After discontinuance of lime neutralization on day 76, the volatile content of the suspended solids increased in both units. Note that after the filter was drained (day 110), the suspended solids concentration in the reactor samples were in the same range as in the effluent from the unit, except for an accumulation of solids in the space below the media in the unit.

Analyses made on tap samples from the filter and upflow bed are illustrated on Figure 8-5. These analyses were made to determine the concentration profiles of volatile acids and TOC in the units. As can be noted from the figures, the concentrations were fairly uniform throughout the depth indicating the units were well mixed.


NOTE:
NOT TO SCALE.
EFF. + RECYCLE LINE
SPRAY PUMP SUCTION
242.5
178.0
-3.6
HEIGHT-cm
7
6
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2
1
SAMPLE TAP (TYP.)
CONE
24 cm H
INFLUENT
270.5
240.0
209.5
179.0
148.5
118.0
87.5
57.0
26.5
8.7
0
FLUIDIZED BED
WEIR
TOP OF MEDIA
MEDIA SAMPLE PORTS (TYP.)
247.0
125.1
64.8
19.1
0
348.0
325.2
276.9
231.8
186.1
155.6
125.1
95.3
64.1
33.7
11.4
0
ANAEROBIC FILTER
GAS
WEIR
GAS
SEPARATION ZONE
348.0
338.0
307.5
302.5
267.0
259.1
228.6
198.1
167.6
137.2
106.7
76.2
45.7
14.6
0
UPFLOW BED

Figure 8-3. Pilot plant sampling tap locations.

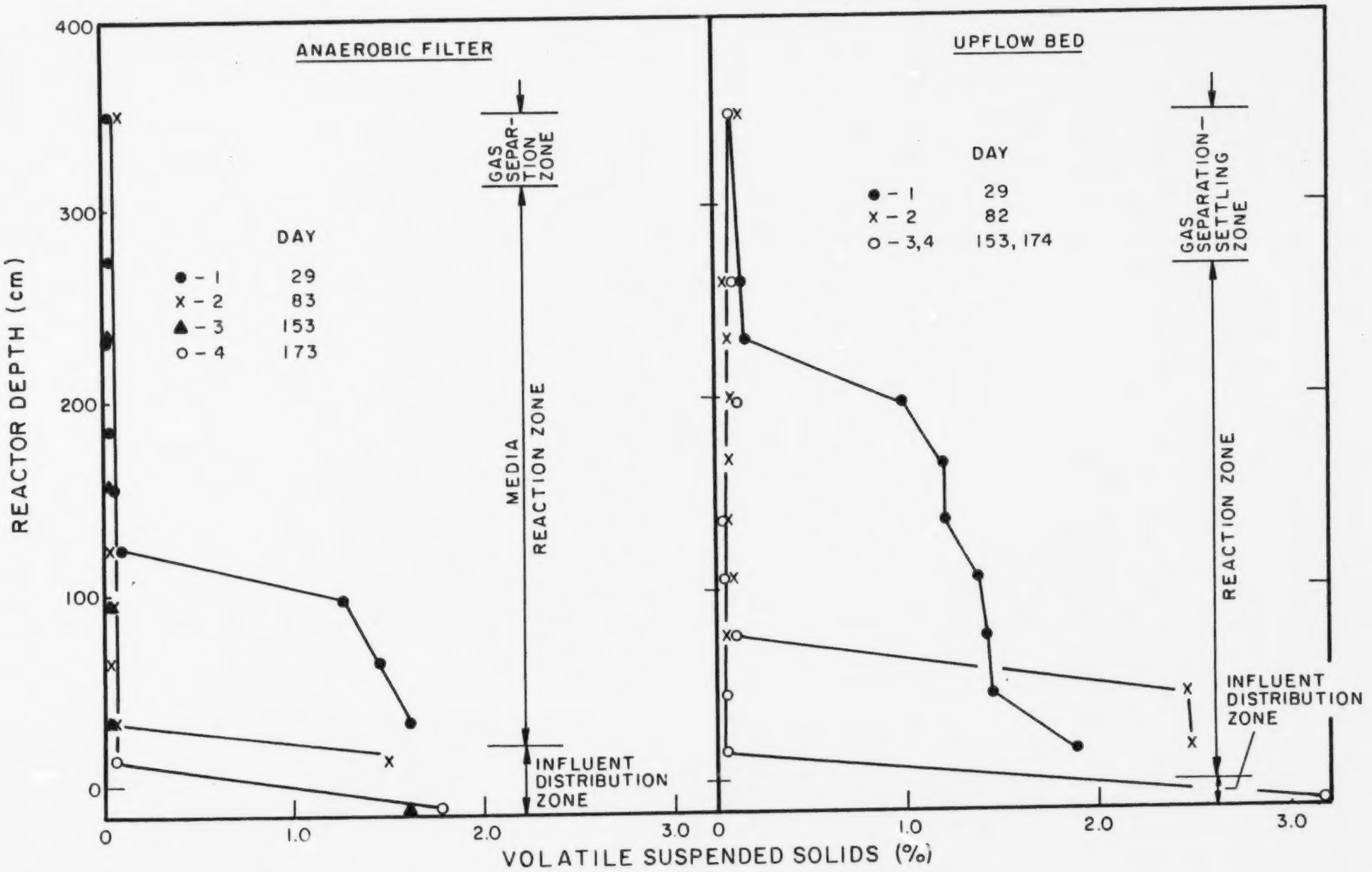


Figure 8-4. Pilot plant volatile suspended solids profiles.

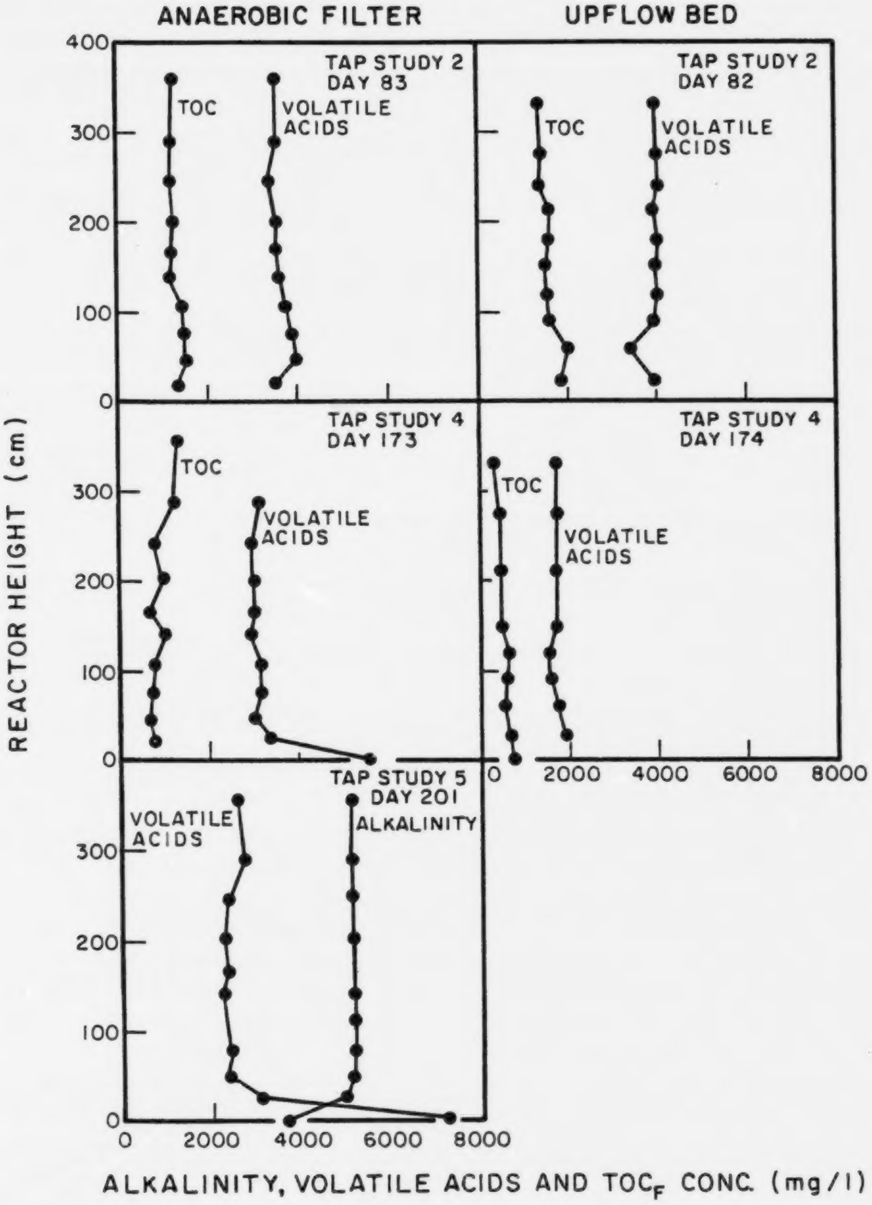


Figure 8-5. Pilot plant depth profiles.

Tap study 5 on the filter was conducted with no recycle flow during the last week of the study. High volatile acids and low alkalinity were found at the bottom of the unit; however, gasification apparently quickly mixed the incoming waste with the reactor contents. The COD removals during this period of no recycle at a loading of about 24 kg/m^3-d were consistent at 75 to 80 percent, indicating no detrimental effect of no recycle under these conditions.

TABLE 8-1. TAP STUDIES SUSPENDED SOLIDS IN ANAEROBIC FILTER AND UPFLOW BED

Tap Study Number	Day	COD Load kg/m^3-d	Flow Q l/d	Recycle R l/d	SS g	VSS g	Percent VSS
Anaerobic Filter							
1	29	2.1	180	18300	9840	6580	66.9
2	83	8.6	850	9000	7560	2510	33.2
3	153	10.4	1150	8000	3060	1560	51.0
4	173	19.1	1670	8000	1830	1180	64.15
5	201	23.9	2290	0	(solids not measured)		
Upflow Bed							
1	29	2.6	190	12300	24100	14600	60.6
2	82	5.7	550	6900	31900	9050	28.3
3	152	5.3	509	8000	(bottom tap not sampled)		
4	174	4.6	430	0	5530	3500	63.3

Tap study 4 was conducted during the period in which the recycle flow in the upflow bed was limited to only that due to recycling sludge, day 153 to 203, to try to promote greater solids accumulation. The sludge recycle flow was approximately two to three times the influent flow. The distribution of TOC and volatile acids indicated mixing throughout the reactor. During this period excellent COD removals were measured in the unit; however, COD removal capacity had been increasing very slowly.

The results of tap sampling of the fluidized bed are shown on Figure 8-6 and summarized in Table 8-2. It was somewhat difficult to obtain a homogeneous sample since both liquid and sand media were collected. Sampling frequency was also limited so as not to significantly reduce bed volatile solids. The sample ports were fixed, and as a result, samples collected close to the sand-sludge interface or near the surface of the bed could have been affected by excess sand or clear liquid, and have caused the variations in solids in the sludge zone shown on Figure 8-6. Samples were analyzed for total volatile solids. Dissolved volatile solids in the fluidized bed effluent were measured in the range of 1000 to 1500 mg/l. For samples from the media part of the bed, the liquid which was generally quite clear, was separated from the sand before analyses. The dissolved volatile solids in the samples analyzed were relatively low, thus, volatile solids measured were essentially all suspended volatile solids.

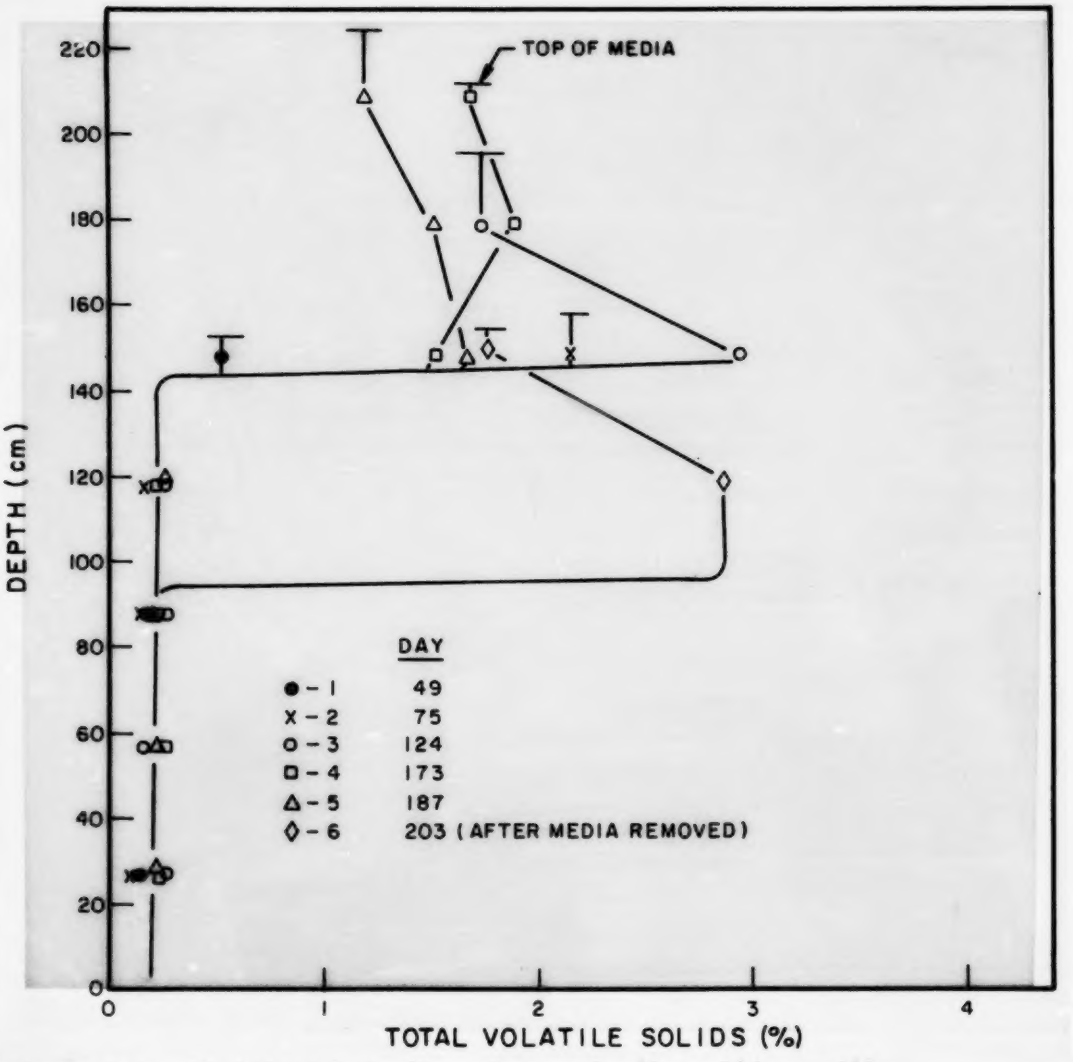


Figure 8-6. Fluidized bed pilot plant volatile solids profile.

TABLE 8-2. FLUIDIZED BED TAP STUDIES SUMMARY OF VOLATILE SOLIDS DATA

Tap Study Number	Day	COD Load kg/m^3-d	Flow l/d	Recycle l/d	Bed Height Sludge Interface cm	Bed Height Total cm	Average % Expansion of Sand Media	TVS g
1	49	6.1	16	13600	-	151	35	76
2	74	5.4	13	13600	143[a]	157	47	99
3	124	25.3	54	13600	143[a]	195	41	276
4	173	41.5	98	12500	143[a]	210	31	282
5	187	46.1	131	10900	147	229	37	290
6	203	74.9	142	9810	91	154	40	340

[a] Estimated (see text).

An interface between lightly coated sand and a layer containing very heavily coated sand particles was observed to occur. Apparently, biological growth built up on the finer sand particles in the upper layer of the media. As growth increased around the sand particle, its density relative to the lightly coated sand below decreased, resulting in the formation of an upper zone in the fluidized bed which contained most of the volatile suspended solids (biological growth). The interface was observed during the later part of the study at 140 to 150 cm depth and remained at about this level. The bed growth and volatile solids accumulation took place above this interface. This upper section increased as loading was increased. The height of the interface up to day 173, prior to its observation, was estimated to occur at approximately 143 cm, based on observations of the sand height and recycle rate.

Toward the end of the study, on days 186 and 189, 30 cm of expanded sand media was withdrawn each day from the bottom of the bed to permit the development of a greater depth of the heavily coated sludge section. This eliminated the necessity of sludge wasting, since the total bed height had been approaching the effluent takeoff point. This is illustrated in Table 8-2 by the results from day 203. The interface was observed at 91 cm. The top of the bed was at 154 cm resulting in a sludge zone of 63 cm. Table 8-2 lists the COD loading at the time of sampling, and the calculated total volatile solids in the bed based on the tap sample measurements.

At the end of the study detailed measurements of total volatile suspended solids in the pilot plants were conducted. Figure 8-7 compares the volatile suspended solids profiles in the three units.

The filter pilot unit was drained from each successive tap, top to bottom, and the total volume for each tap was sampled and measured for total and volatile suspended solids. These results are shown in Table 8-3. Some settling of solids may have occurred; however, gasification in the lower sections may have kept most of the solid suspended. Based on comparison of measured liquid volume and total empty bed volume, the average void volume in the filter was calculated as 78 percent. This can be compared with the 97 percent void volume with clean media. Volatile suspended solids were 75 percent of the total

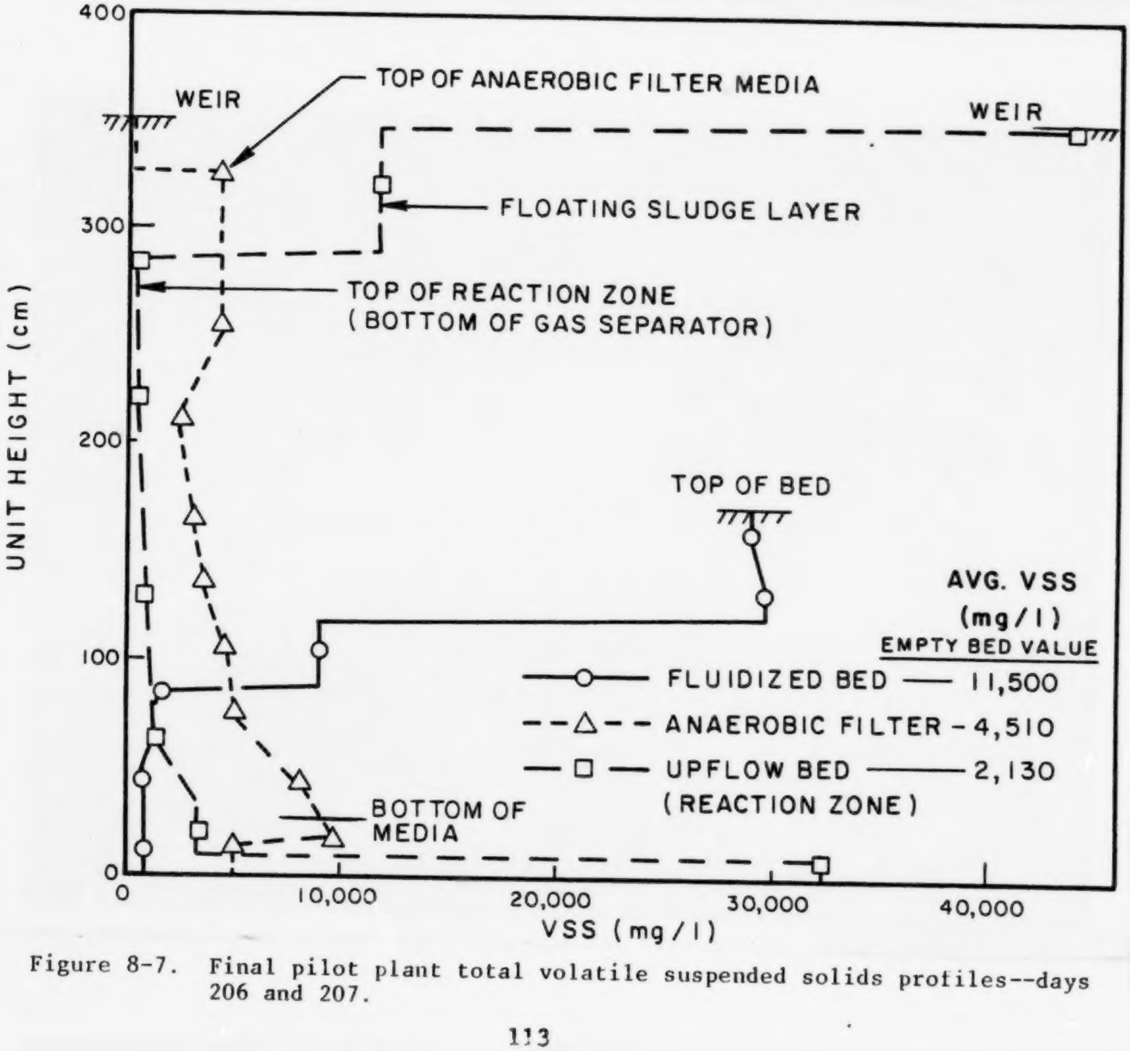


Figure 8-7. Final pilot plant total volatile suspended solids profiles--days 206 and 207.

TABLE 8-3. ANAEROBIC FILTER SOLIDS ANALYSES--DAY 207

A. Suspended Solids

Sample[a]	Measured Liquid Volume Drained-l	Calculated Empty Bed Volume l[c]	% Voids	TSS mg/l	VSS mg/l	% VSS	Total VSS gms
Weir to top of media	71	78	100	80	64	80	4.5
Top to Tap 9	151	212	71	204	168	82	25.4
Tap 9 to Tap 8	151	198	76	436	328	75	49.5
Tap 8 to Tap 7	159	201	79	372	312	84	49.6
Tap 7 to Tap 6	121	134	90	612	488	80	59.0
Tap 6 to Tap 5	98	134	73	596	492	83	48.2
Tap 5 to Tap 4	102	131	78	860	620	72	63.2
Tap 4 to Tap 3	97	137	71	1200	808	67	78.4
Tap 3 to Tap 2	98	133	72	1580	1160	73	114.
Tap 2 to Tap 1	72	98	73	2920	2200	75	158.
Tap 1 to Bottom	108	108	-	7000	5120	73	553.
Total Unit	1228	1564[b]	-	-	-	-	1203
Average (suspended)	-	-	78	1310	980	75	-

B. Solids Attached to the Media

Location of Sampling Point	Height from Media Bottom cm	Total[d] No. of Media	Scale Particles > 1 mm g/media	TSS g/media	VSS g/media	Total VSS gms	Conc. of VSS[c] mg/l
Top of Media	306						
Upper Port	228	408	21.6	5.15	3.41	1390	4110
Middle Port	106	636	18.4	4.11	2.53	1610	3010
Lower Port to	46	315	8.1	5.62	3.57	1130	4290
Media Bottom	0						
Total Media	306	1598	-	-	-	5500	-
Average (attached)	-	-	15.1	5.76	3.44	-	4090

[a] See Figure 8-3 for location.

[b] Volume empty media zone 1486 liters. Total volatile suspended solids in media zone 6700 gms. Average concentration based on empty media zone.

[c] Liquid volume empty bed basis 4.39 l/cm.

[d] Between sampling points.

suspended solids. As can be noted, the concentration of solids in suspension increased near the bottom. This may have resulted from solids settling during sampling or the tendency of heavier settleable solids to gradually buildup in the lower section of the bed. The suspended solids concentration was higher than measured in the previous tap study, possibly due to some detachment from the media during sampling and draining. (Note that the unit had been drained due to a line break and much of the suspended solids in the bottom of the unit were lost on day 110.)

After the filter was drained, the media sampling ports were opened and samples of the media were collected. The solids on the media were washed off into a measured volume of distilled water and analyzed for volatile and total solids. Much of the media had a thin coating of scale under the biological growth, some of which broke off during washing. Those particles > 1 mm were screened from the samples before measuring for volatile solids. The volatile solids measured in the liquid and measured as attached to the media, were combined and the total volatile suspended solids in the unit was calculated ignoring dissolved solids in the liquid. The average volatile suspended solids concentration in the filter was about 5070 mg/l. Approximately 80 percent of the volatile suspended solids were measured as attached.

The upflow bed was drained from the bottom of the unit at the end of the study in several increments. The volume was measured and sampled, and the results are shown in Table 8-4. Tap sampling studies during operation indicated that solids above a heavy, settled layer on the bottom were fairly uniformly distributed in the column. Some settling probably occurred during this final sampling as indicated in the gradation of suspended solids in samples two to six. There was a concentration of 3.3 percent volatile suspended solids (sample 1) at the bottom of the unit and a very high concentration of suspended solids, apparently from a floating layer, at the top of the unit (samples 7 and 8).

TABLE 8-4. SOLIDS ANALYSIS - UPFLOW BED--DAY 206

Sample Number	Volume Drained Liters[a]	Height from Bottom cm	TSS mg/1	VSS mg/1	Percent VSS	Total VSS gms
1	50	6	50,500	32,900	65	1640
2	125	26	4950	3680	74	460
3	250	68	114	850	74	213
4	375	139	845	625	74	234
5	375	225	630	460	73	173
6	125	281	470	350	75	44
7	125	309	21,600	11,700	54	1460
8	7	324	203,000	44,000	22	307
Average[a]	1300	267	-	2130	68	2770

[a] Active zone 1300 1, samples one to six.

The % volatile content of the suspended solids in the upper layers was relatively low and therefore, they were assumed to be relatively inactive. Based on the configurations of the gas separation section, it was assumed that these suspended solids had been trapped in the gas separation cone and were not in active contact with the waste. Unfortunately, the unit was drained prior to opening the top to permit observation of this floating solids layer. A modified gas cone, to permit trapped solids to wash over the weirs should be incorporated into the design of the unit for subsequent studies. Excluding the top layer of solids, the average active volatile solids concentration in the unit (samples 1 to 6) was 2130 mg/1, however, above a depth of approximately 40 cm, the average concentration was in the range of 600 mg/1.

The fluidized bed was sampled at the taps starting at the top of the reactor bed, removing the total bed contents. The bed was fluidized during sampling. Water was added to the unit to replace the volume removed after each tap was sampled and the recycle rate was reduced to maintain the bed height at the corresponding level and at about the same percent expansion. The suspended and volatile suspended solids were determined on each sample and the results are shown in Table 8-5 and on Figure 8-7.

TABLE 8-5. FLUIDIZED BED SUSPENDED SOLIDS--DAY 207

Sample	Total Bed Volume l[b]	VSS mg/l	Sand and[a] Inerts gm/l	Total VSS gms
Top of Bed to Tap 5	4.6	28,500	14.8	131
Tap 5 to Tap 4	5.5	29,600	23.4	163
Tap 4 to Tap 3	5.5	9,150	390	50.3
Tap 3 to Tap 2	5.5	1,660	1230	9.1
Tap 2 to Tap 1	5.5	910	1630	5.0
Tap 1 to Bottom	5.0	1010	1530	5.0
Total	31.6	-	-	363
Average	-	11,500	-	-

[a] Total sand in bed 25,700 grams.

[b] Total bed depth 173 cm, volume 31.6 liters, sand sludge interface measured at 91 cm depth.

Approximately 80 to 85 percent of the total bed volatile suspended solids accumulated in a sludge zone above the lightly coated sand. This zone contained relativly little sand. The overall average volatile suspended solids concentration in the total bed was about 11,500 mg/l, and in the sludge zone the concentration of volatile suspended solids was approximately three percent.

The COD removal rate per unit volatile suspended solids for each of the units, based on the measured final volatile suspended solids and the measured COD removal during the final three to five days of operation is shown in Table 8-6. It is interesting to note that although there is a significant difference in volumetric removal rate between the filter and fluidized bed, COD removal per unit volatile suspended solids, effluent COD concentration, and percent COD removals are quite similar. The lower loaded upflow bed produced a lower effluent COD concentration and higher percent COD removal at the lower removal rate, which is consistent with kinetics of biological degradation. The removals of 1.8 to 4.3 kg COD/kg volatile suspended solids-day and final effluent COD levels, can be compared to aerobic systems in which typical COD removals are in the 0.4 to

0.6 kg COD/kg volatile suspended solids-day range, to achieve 90 percent COD removal, and an effluent concentration of 100 mg/l or less, biodegradable COD.

TABLE 8-6. COD REMOVAL RATES
(Based on Reactor Volume and Reactor Volatile Solids at End of Study)

Unit	Period Days	COD Removed kg/m^3-d	Total COD Removed kg/d	Percent COD_R	Effluent COD mg/l	Total VSS in Unit kg	Removal kg COD_R/kg VSS-d
Filter	204-206	18.9	25.5	75.7	3370	6.70	3.8
Upflow Bed	197-202	4.4	5.1	89.9	1480	2.77	1.8
Fluidized Bed	203-207	52.4	1.56	77.7	3330	0.36	4.3

HALF DEPTH STUDY ANAEROBIC FILTER

The concentration profiles measured during operation, and the tracer studies indicated good mixing of the wastewater in the anaerobic filter unit. The pilot plant reactor depth was three meters. Typical filter design for economic reasons is in the range of 6 to 10 meters. It was desired to determine where in the reactor removals were taking place, and if there were unproportionally high removals in the bottom section of the filter, where settleable solids and possibly heavier attached growth might accumulate. Observation of the data on the pilot units clearly indicated that at any given point in time, a significant abrupt change in loading was reflected in the subsequent effluent volatile acids concentrations. This is consistent with removal rate and growth kinetics. Thus, adjustment of the flow (loading) to the filter to yield a fairly constant effluent volatile acid concentration, with measurement of the COD removed, should provide an estimate of the unit's removal capacity at that point in time (over several consecutive days). Changes in capacity due to growth accumulation was observed to be relatively slow in the anaerobic filter; thus over several days of testing, changes in the active volatile biological solids in the unit were assumed to be low.

The filter was drained to approximately mid-depth (tap 5). Effluent was then taken off at tap 5; and the media was submerged to tap 6 by the effluent piping arrangement to provide a gas trap. This resulted in a wetted volume of 45 percent of the total media volume in the pilot unit. The filter was run in this mode from day 187 to day 196. The flow was decreased to the unit until effluent volatile acids were in the 2000 to 2500 mg/l range, typical of the operation of the unit prior to volume reduction. This required approximately five days, and data from day 192 to 196 were analyzed as representative of the lower half removal capacity.

The unit was then refilled and the flow was increased to result in the same COD loading based on volume, on the total unit as during the half depth period. Data prior to the test, day 176 to 179; during the test, day 192 to 196, and following the test day, 199 to 206, are shown in Table 8-7. The volumetric loading to the half depth section was increased almost 50 percent above that previously (176 to 179) on the full depth; however, volatile acid concentrations increased and COD removals were lower. This indicated a greater COD removal capacity by approximately 35 percent in the lower section. Some increase was probably due to an increased removal rate associated with the higher loading and volatile acid concentrations. The loading after the unit was refilled (199 to 206) was maintained at about the same level as during the half depth period. Similar effluent volatile acid concentrations and COD removals were observed, and the results (Table 8-7), are indicative of equal removal capacity in the upper and lower halves of the filter.

The final suspended solids profile, previously presented, indicated higher volatile solids in the bottom sections of the filter. The average data indicates the lower section, below tap 6, contained about 60 percent of the volatile suspended solids, and therefore, it might be expected to have somewhat greater removal capacity than the upper half. Although the results indicate a 50 percent split in capacity, the accuracy of measurements and possible settling of suspended and loosely attached solids during draining and sampling, may have caused some shift in removal capacity from the top to the lower section. It is felt that this study indicates that the upper section of the unit was removing a significant portion of the COD, and that it would probably be reasonable to scale up to a full scale unit 6 to 10 m in depth. Some conservatism, however, would be justified until further longer term studies, with depths up to full scale, provide more definite data.

TABLE 8-7. COMPARISON OF ANAEROBIC FILTER TOTAL REACTOR VERSUS BOTTOM SECTION OF REACTOR

Description	Total Reactor (before)	Bottom Section	Total Reactor (after)
Period	Day 176 - 179	Day 192 - 196	Day 199 - 206
Influent flow l/d	1560	1100	2260
COD mg/l	14200	13300	14400
Media volume m^3	1.345	0.600	1.345
Loading rate kg COD/m^3-d	16.5	24.4	24.2
Effluent COD mg/l	2720	3290	3270
Volatile Acids mg/l	1800	2290	2270
Gas l/g COD_R	0.43	0.45	0.38
Percent COD Removal	80.8	75.3	77.3
kg COD removed/m^3-d	13.3	18.4	18.7

Removal capacity of bottom section of reactor to total reactor, considering pre-study period = 17.9/13.3 = 1.35, and post study period = 17.9/18.0 = 0.99.

CONDENSATE 24 HOUR COMPOSITE INFLUENT STUDY

As previously indicated, raw condensate was collected during full operational periods of the evaporator, excluding wash periods. Normally there are three wash cycles per day. The waste was characterized during two compartment wash periods. The results were similar for both periods. Table 8-8 illustrates the June sampling period. As can be noted, a heavy carryover of sulfite liquor with high COD occurs during the first 10 minutes at the beginning of the two hour wash period. The COD of the wash

TABLE 8-8. ANALYSIS OF GRAB SAMPLES DURING EVAPORATOR COMPARTMENT NO. 8 WASH--JUNE 9, 1983

Parameters	Sulfite Liquor	Sample Identity FCG-1	FCG-2	FCG-3	FCG-4	FCG-5	FCG-6	FCG-7	FCG-8	FCG-9	FCG-10	FCG-11	FCG-12
Sampling Time[a] (min)	-27	-6	2	3	6	9	14	20	30	45	60	87	-
pH Unit	4.18	2.25	2.64	2.53	3.85	3.45	3.25	3.07	2.96	3.25	2.96	3.0	2.5
Acidity (mg/l as $CaCO_3$)													
to pH 4	-	1610	1580	1510	436	996	1220	1350	1350	1180	1270	1350	1490
to pH 7	9730	5510	6460	6180	6540	6090	6080	6250	6470	6240	6430	6470	6700
to pH 8.3	14100	5990	6970	6660	7420	6540	6540	6660	6680	6640	6870	6800	7160
Volatile Acids mg/l	14600	5850	7330	7000	9160	7640	7280	7360	7690	7590	7750	7690	7810
COD mg/l	96700	10700	12600	12000	39300	20500	6470	9820	12100	14300	13000	13100	13300
Sulfate mg/l	125	28	18	40	1120	245	40	34	3	3	5	18	29
Sulfite mg/l	1550	666	530	530	340	285	260	155	305	105	430	440	440
Sulfide mg/l	0	12	17	55	13	50	18	46	16	19	9	8	7
Total Solids mg/l	148000	204	144	198	24600	6610	1630	598	602	662	474	444	310
Total Volatile Solids mg/l	96100	116	82	152	21000	6330	1520	518	526	338	404	156	1180
Color - PCU	75000	20	20	60	15000	4000	1200	320	400	240	240	240	30

[a] Wash started at T = 0.

water was about the same as during full evaporator operation after the initial surge; however, the color of the wash decreased gradually remaining above prewash levels through the first hour.

During the final several days of operation, the fluidized bed was fed a simulated 24 hour composite waste sample to determine if an acute toxic effect on the system would be caused by constituents in the liquor at one percent concentration level. The waste was prepared by adding one liter of condensate sample collected at the beginning of the wash cycle to each 100 liters of regularly collected influent waste to represent a one percent concentration in a 24 hour equalized sample. Table 8-9 presents average results during day 204 to 207.

TABLE 8-9. FLUIDIZED BED SIMULATED 24 HOUR INFLUENT COMPOSITE WASTE DAY 204-207

Parameters	Results
Influent	
- Flow 1/d	126
- COD concentration mg/1	15500
- Color PCU	900
Loading rate kg COD/m^3-d	68.7
Effluent	
- COD concentration mg/1	2500
- Acids concentration mg/1	1600
- Color PCU	3600
Gas produced 1/g COD_R	0.54
Percent COD removal	83.9

The COD of the feed was essentially the same as had been previously fed to the unit. The color increased to 900 units compared to 600 units. Effluent color from the fluidized bed increased to 3600 units from 1600 to 2000 color units measured prior to this study; however, COD removals were not detrimentally effected. Although this study was run only for a relatively short time, it indicated there was no immediate toxic effect on the fluidized bed performance, due to addition of the wash water to the condensate at a one percent concentration.

SIEVE ANALYSES OF FLUIDIZED BED MEDIA

Table 8-10 presents results of sieve analyses conducted to characterize the sand media from the fluidized bed unit. The sand from the bed was sieved after the attached volatile suspended solids had been burned off.

TABLE 8-10. SIEVE ANALYSES OF SAND SAMPLES FROM FLUIDIZED BED

Sample[a] -	Tap 1	Tap 1	Bottom	Tap 1	Tap 2	Tap 3
Date -	7/12	7/15	8/3	8/3	8/3	8/3
Day Number -	186	189	208	208	208	208
Bed Depth - (cm)	229	211	175	175	175	175
Sieve Size mm	Percent by Weight Greater Than Size					
> 0.84	0.9	0.9	< .1	< .1	< .1	< .1
0.59	20.2	17.7	16.1	17.0	16.6	1.1
0.50	62.3	63.3	52.0	53.2	52.1	3.4
0.42	91.0	93.8	80.4	82.5	81.4	16.2
0.35	99.1	99.4	95.6	96.8	96.2	58.4
0.30	99.8	99.8	99.5	99.9	99.8	92.0
0.15	99.9	99.9	99.6	100	99.9	99.6
0.10	100	100	100	-	100	99.7
< 0.10	-	-	-	-	-	0.3
50% Size	0.54	0.54	0.50	0.50	0.50	0.37
Effective Size	0.43	0.43	0.39	0.40	0.40	0.32
Uniformity Coefficient	1.3	1.3	1.3	1.3	1.3	1.3

[a] See Figure 8-3 for tap locations.

Samples were collected from Tap 1 where sand was removed from the bed, as previously discussed and from all of the taps at the end of the study. The results of the July 12 and July 15 analyses were consistent, and showed a slightly higher average particle size than the samples at the end of the study. The accumulation of the smaller size particles at the top of the bed can be seen in the Tap 3 results. Most of the sand, over 90 percent by weight, was between 0.3 and 0.6 mm, with an average size of about 0.5 mm. The effective sand size was approximately 0.4 mm and the uniformity coefficient 1.3.

SHUTDOWN/STARTUP

Waste was not available for several days during the annual shutdown of the evaporator for cleaning and repairs. The pilot plants were operated on recycle only and when waste was available again, flows were increased to former levels. Data on loading, gas production and effluent volatile acids during this period for each of the pilot plants are shown on Figure 8-8. Volatile acids and COD concentrations (the recycled flow) for each unit dropped within the first day of no load. The volatile acid concentration in the recycled flow remained fairly constant during the following two days of no load. The filter, fluidized bed, and upflow bed volatile acids averaged 507, 562, and 309 mg/l, respectively, during the three days of recycling. The COD_F in the recycle averaged 1270, 1500, and 1030 mg/l, respectively. Gas production had dropped off from very low to non-measurable levels by the third day of no waste feed. These results would indicate maximum attainable COD removals of 91, 89 and 93 percent, respectively, in each of the units at the previous loadings, (influent COD = 14,200 mg/l) and unit solids levels. As can be observed, gas production responded as loading was brought back and the units were at previous loadings and removals within a few days. The COD removals as shown on the chronological plots in Section 7, returned to previous levels.

DATA CORRELATIONS

The primary measure of organic load and removal was COD of the influent and filtered effluent. In addition, measurements of BOD, TOC and volatile acids were made on the influent and effluent. Figures 8-9 and 8-10 show the correlations between total influent COD and soluble effluent COD and these parameters. The correlation of effluent COD with the volatile acids

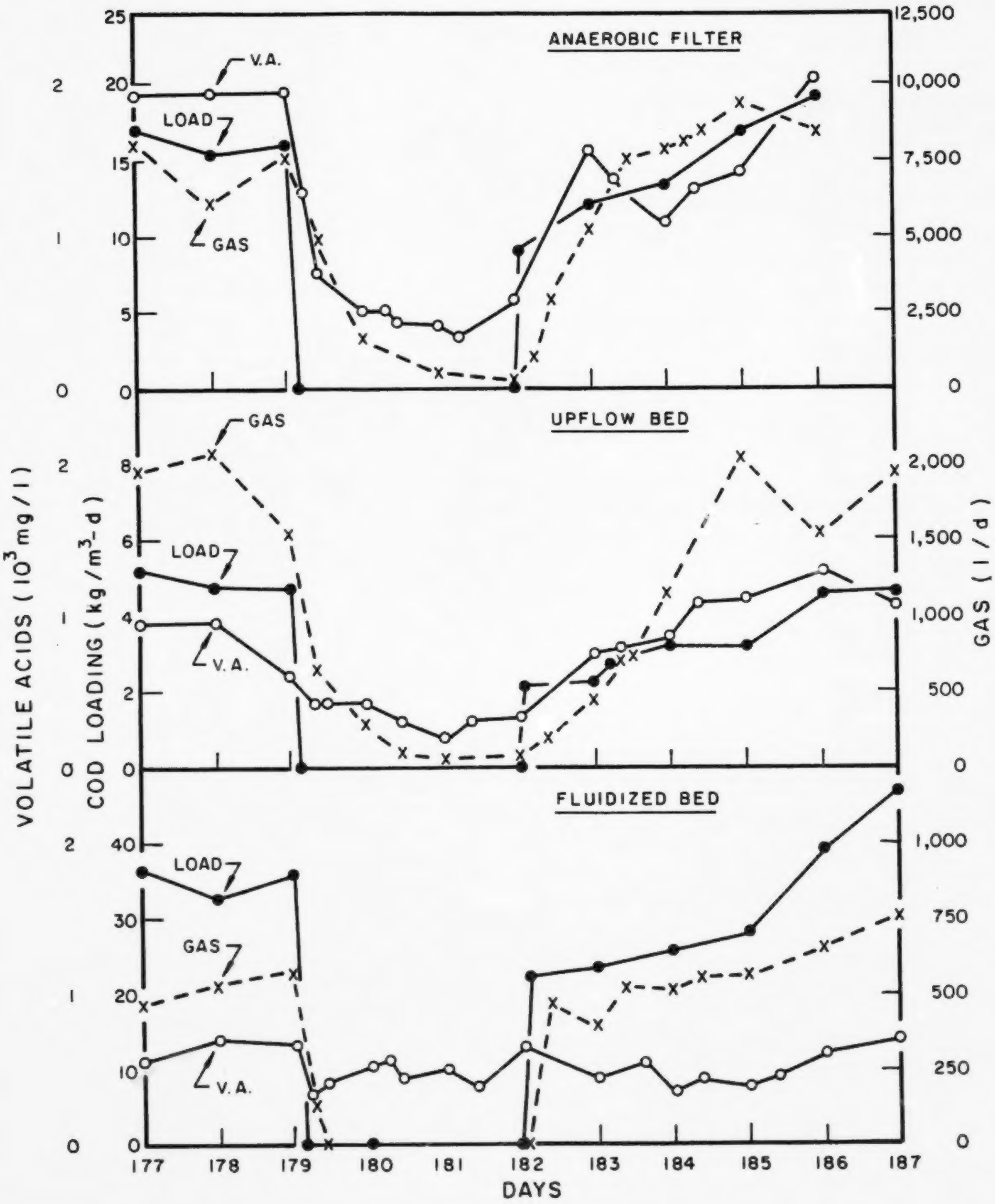


Figure 8-8. Pilot plant chronological data during shutdown and re-startup.

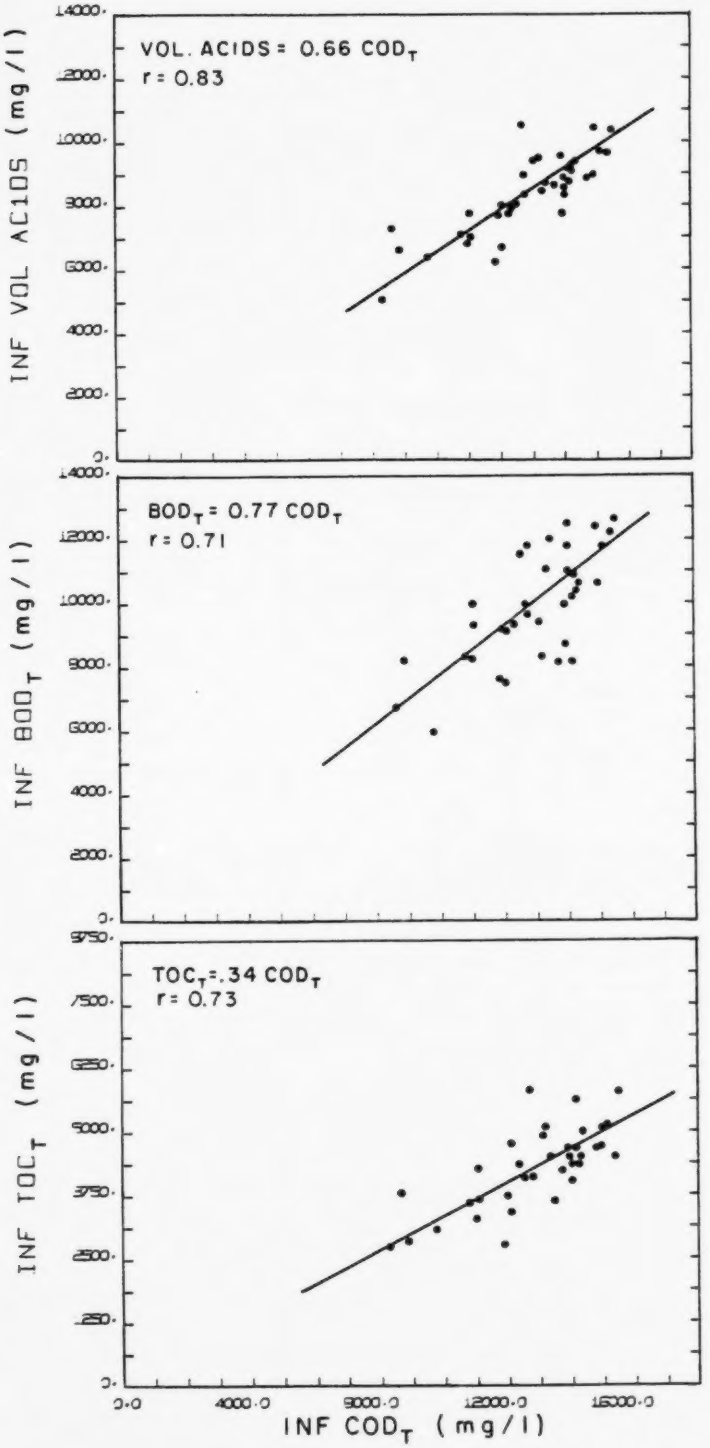


Figure 8-9. COD data correlations influent waste.

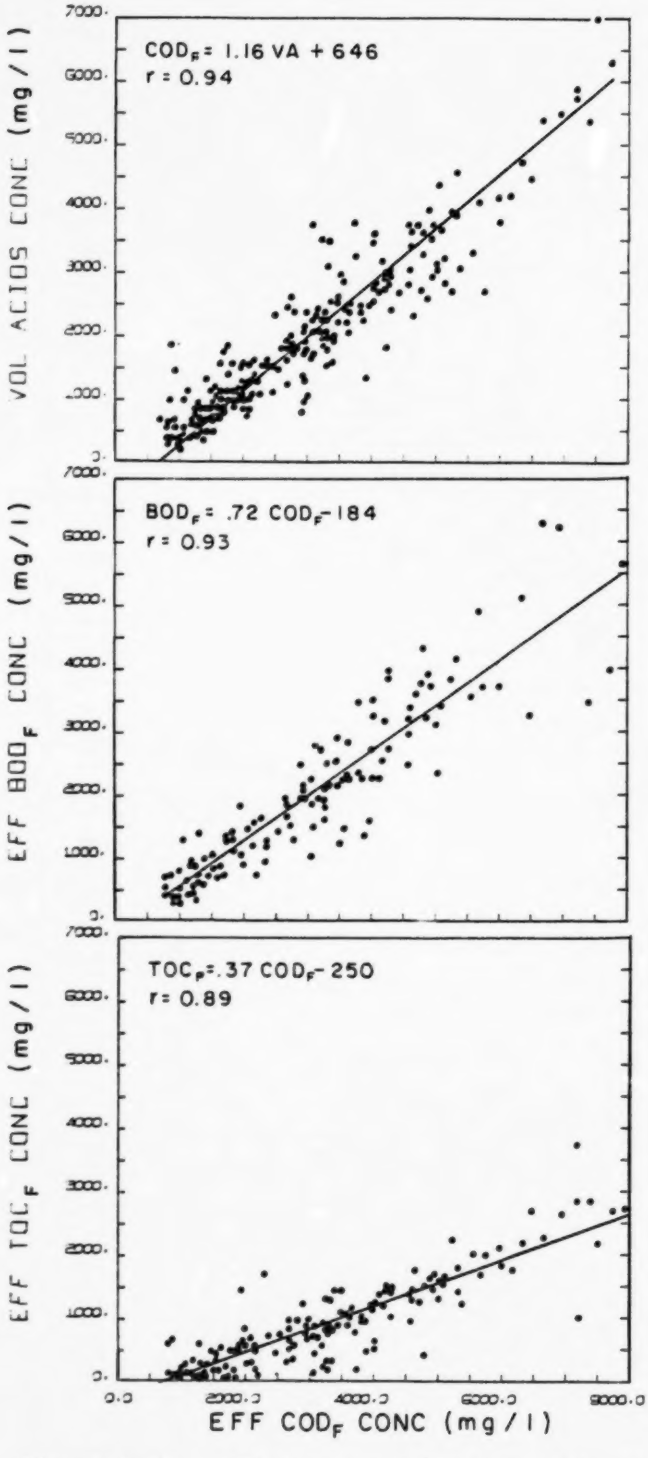


Figure 8-10. COD data correlations effluent.

was very good; therefore, volatile acids measurements, which were conducted daily and which were determined by a relatively quick and simple test, were used to monitor the pilot plant operations on a daily basis. Figure 8-11 illustrates total and volatile suspended solids relationships during the latter half of the study, after use of lime which caused scaling was discontinued. Based on volatile suspended solids production in the units total suspended solids production can be calculated.

GAS PRODUCTION AND SOLIDS PRODUCTION

Gas measurements were made using factory calibrated wet test meters. The meter gas readings were corrected to standard temperature and pressure based on measured temperatures in the reactor and an average barometric pressure calculated for the plant site elevation. The meters were also compared to each other using the gas from one pilot plant. One meter had to be shared between the filter and fluidized bed until day 75, because the meter supplied with the fluidized bed, was returned to the factory for repair of a small leak.

During the study, on days 75, 138, 167, and 206, the meters were checked, and the meter liquid levels were adjusted. Generally, oil was added to the filter and upflow meters (to make up evaporation losses due to high gas flow) and liquid was removed from the fluidized bed meter (condensation of water). The change in instantaneous gas measurements over a period of a few minutes prior to and following the adjustments were:

	Percent Change in Reading after Adjustment		
Day	Filter	Upflow	Fluidized Bed
75	+ 3.0	- 20.0	New meter
138	+ 3.5	+ 1.8	- 3.7
167	+ 31.3	+ 25.7	- 1.7
206	+ 35.5	+ 31.0	- 11.1

The pilot plant total gas production as related to COD removal, was variable due to loading, removal variability, and gas content. A review of the data prior to and following the adjustments, however, indicated that

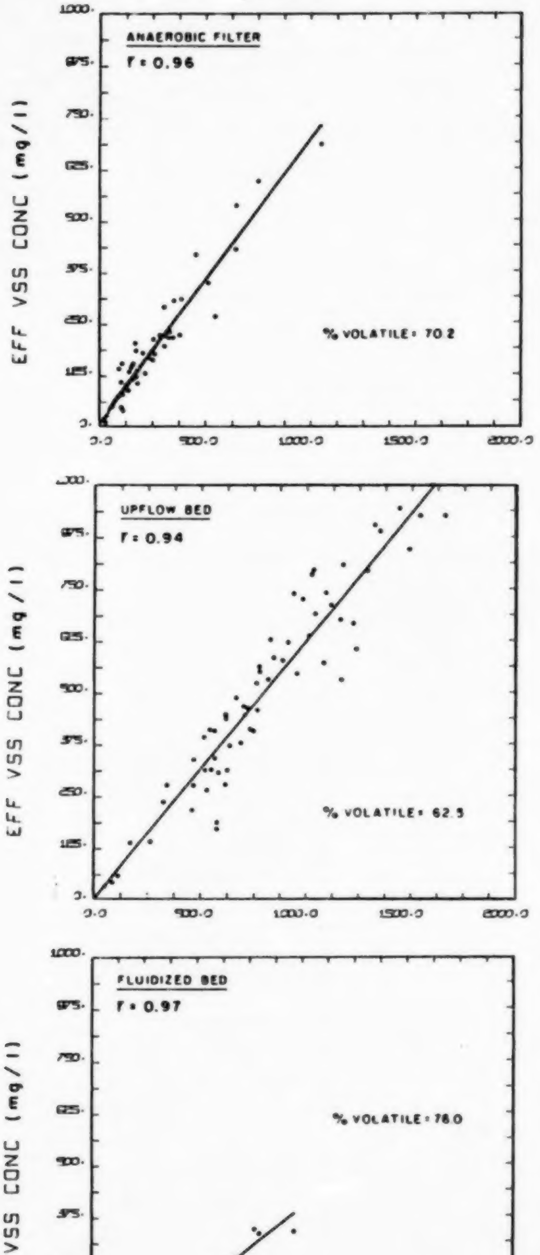


Figure 8-11. Effluent suspended solids-volatile suspended solids correlation--Day 100-207.

the long term effect of the adjustments on the gas/COD ratio was minor compared to that indicated by the short term measurements shown above. It was therefore concluded that the effect of the adjustments were not as drastic as may seem from the above short term measurements. Gas to COD ratios for the upflow unit for days 199 to 202 averaged 42 percent of the average data, over the period of day 46 to 199. The ratio for the filter for days 204 to 206 averaged 64 percent of the average data. There was no apparent reason for these low values determined, and the data were not included in the overall data averages.

Figure 8-12 presents chronological gas production plots for each of the three reactors during the study. Data during startup and initial loading up to day 46 were not included. Daily data values greater than 950 l/kg COD_R or less than 50 l/kg COD_R which occurred when a unit was under or over fed were not included in these plots. Two, eight and four values for the fluidized bed, upflow bed, and filter, respectively, were eliminated. Typically, when the pilot unit influent was reduced due to high volatile acids, the COD removed, based on influent to effluent data, would not include the reduction in volatile acids in the reactor volume, and this would distort the gas to COD ratio for that day. Similarly, on a startup or loading increase day, the gas production ratio usually would be low due to a buildup in volatile acid concentration in the reactor. Although there was quite a bit of variation from day to day due to loading factors, and due to pH variations, the overall average gas production averaged out in the range of 0.4 to 0.5 liters per gram of COD removed, for each of the pilot units, as shown below:

Unit	Average Gas Production l/kg COD_R	Average Percent CH_4	Average Methane l/kg COD_R	Calculated Volatile Suspended Solids Yield kg/kg COD_R
Filter	464	68.1	316	.024
Upflow Bed	458	68.3	313	.027
Fluidized Bed	483	67.5	326	.017

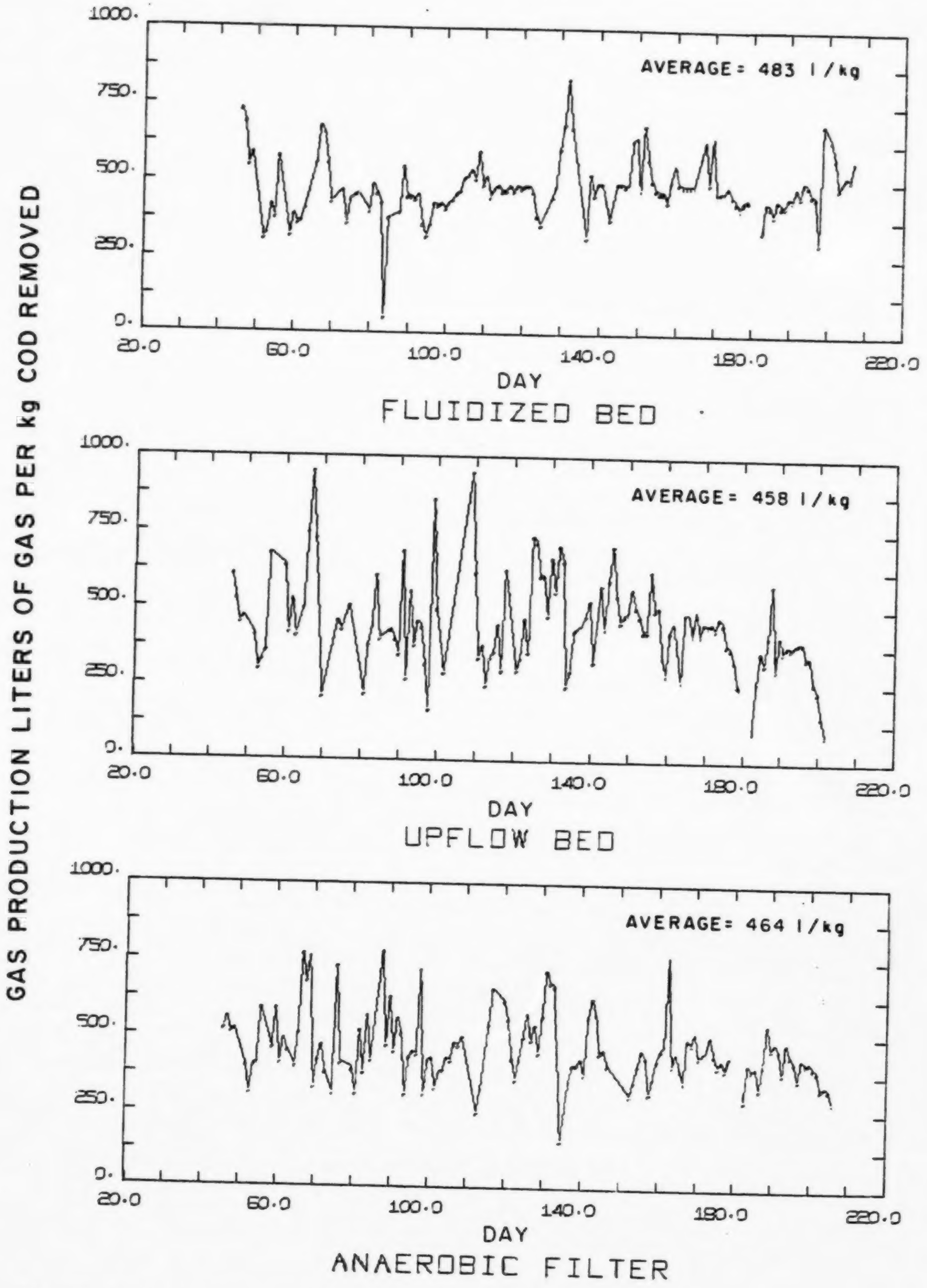


Figure 8-12. Pilot plant daily gas production.

Since suspended solids were continually being retained in the systems and were not easily measurable, a COD balance was used to determine a rough estimate of suspended solids production. The volatile solids yield was calculated based on the difference between a theoretical 0.35 liters methane per gram COD and the actual average gas production measured. A typical value of 1.4 gram COD per gram volatile suspended solids was used to convert COD to volatile solids. The net solids yields determined are consistent with literature(1) yield coefficients of 0.04 to 0.05 for anaerobic treatment of acetate, and also allow for some decay in anaerobic digestion. The values are somewhat lower than the volatile solids yield calculated in a similar manner(2) of 0.08 to 0.09, for a similar waste.

pH--ALKALINITY

The pH in the anaerobic reactors was a function of alkalinity, volatile acid concentration, and carbon dioxide present. Figure 8-13 illustrates the percent methane measured in the gas compared to reactor pH. Carbon dioxide which was also measured in the gas, made up most of the remainder of the gas. Hydrogen sulfide content was calculated and amounted to one half to two percent of the gas. The combined value for CO_2 and H_2S shown on the figure are the difference between 100 percent and methane measured. Alkalinity addition to the raw waste was generally constant during the study; thus variations in pH within the reactor were primarily a function of the volatile acid content. As the volatile acid concentration increased due to an increase in load, or a loss of removal capacity, bicarbonate alkalinity and pH in the reactor decreased. A greater percentage of CO_2 was then measured in the gas, since less was in the form of bicarbonate in solution. The relationship between calculated bicarbonate alkalinity (total measured alkalinity minus measured volatile acid alkalinity) and pH measured during this study is shown on Figure 8-14. The curve through the data is a theoretical curve(3) based on the equilibrium for CO_2 gas concentration and pH. The CO_2 concentration from Figure 8-13 was used. Most of the pilot plant data were at pH 7.2 to 7.4, and as can be observed, the theoretical curve fits the average results quite well in this range, despite the rather wide range of data.

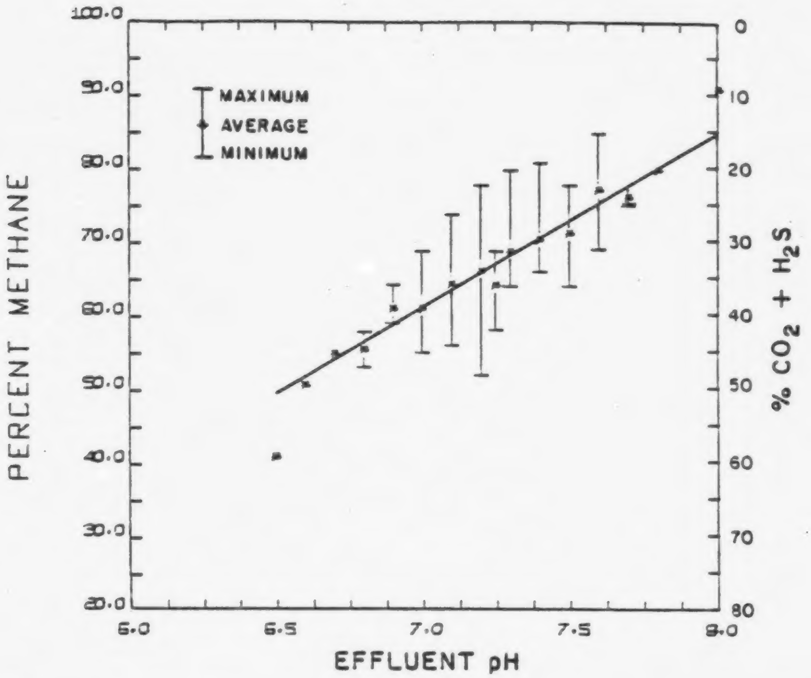


Figure 8-13. Gas analyses methane content-pH relationship.

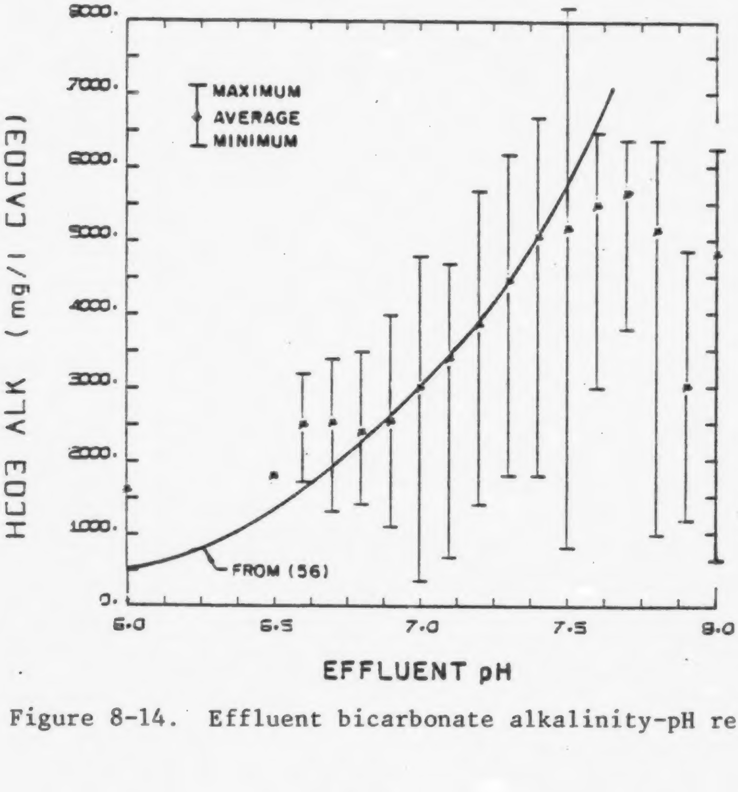


Figure 8-14. Effluent bicarbonate alkalinity-pH relationship.

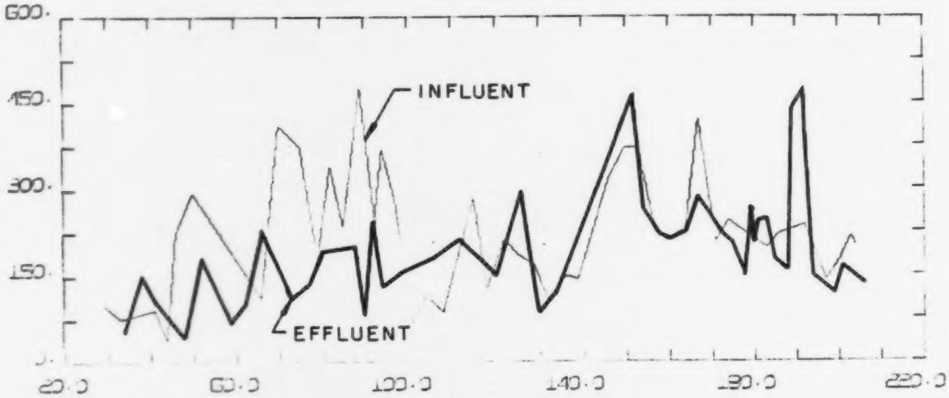
The bicarbonate alkalinity in the reactor is a function of the alkalinity added and the level of volatile acids at which the unit is operated. To minimize alkalinity addition, the unit should be operated at the lower pH range, 6.8 to 7.0 at loadings which will result in minimal volatile acids concentration, at steady state conditions. Maintaining bicarbonate alkalinity around 2000 to 2500 mg/l should maintain pH in the unit at 6.8 to 7.0 range and allow for some deviation due to load variation with operation at volatile acid concentrations of less than 2000 mg/l.

SULFUR--HYDROGEN SULFIDE GAS

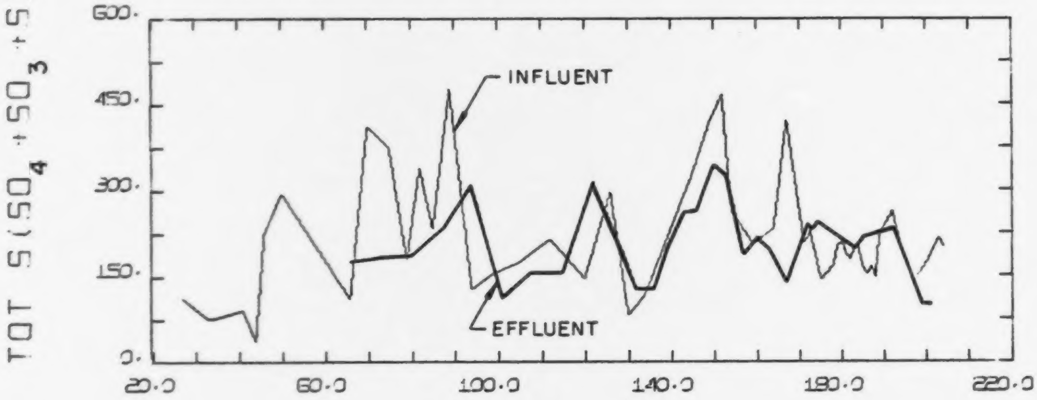
In this study, it was concluded from raw waste and the pilot plant influent data that sulfur compounds in the waste, primarily sulfite, were partially oxidized to sulfate during filling and mixing in the storage tanks. Part of the sulfite and sulfate were reduced in the reactors to sulfides. Figure 8-15 illustrates a chronological plot of total sulfur in the influent and effluent from each of the pilot plants. There was a significant range in sulfur compound concentration in the raw waste (Table 7-1), and relatively low conversion to hydrogen sulfide gas. Influent and effluent data overlap at times due to the detention time lag in the units with some variability due to analytical measurements.

Hydrogen sulfide in the gas was not regularly measured during this study. Based on sulfide and pH measurements of the reactor contents it was possible to calculate theoretical equilibrium concentrations of hydrogen sulfide dissolved in the liquid and in accordance with Henry's law, the concentration in the gas phase.

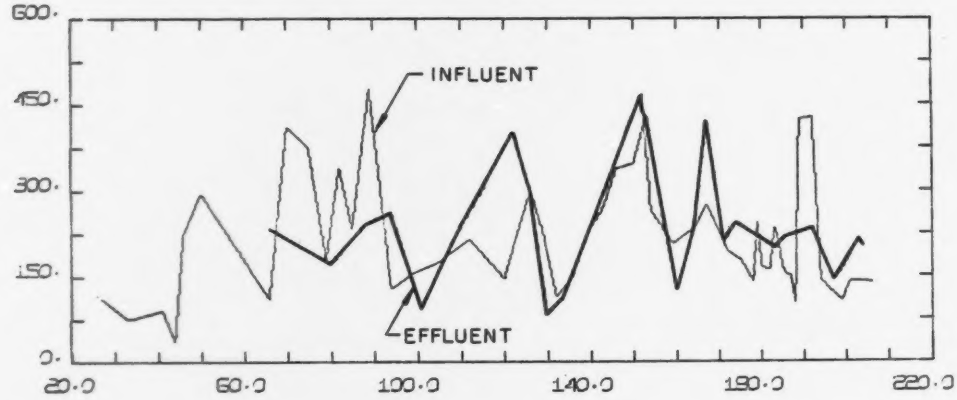
Figure 8-16 shows the theoretical relationships among total sulfide concentration in the reactor, pH, and off gas H_2S concentration at average conditions in the reactor. Based on a typical pH of 7.0 to 7.4 and effluent sulfide concentrations of 30 to 200 mg/l, the range of H_2S concentration in the gas would be one half to three percent. The average H_2S in the off gas, determined for the pilot plant study, was one percent. Figure 8-17 shows the range of H_2S concentration in the gas as a function of reactor pH for this study.



FLUIDIZED BED



UPFLOW BED



ANAEROBIC FILTER

Figure 8-15. Chronological data influent-effluent total sulfur.

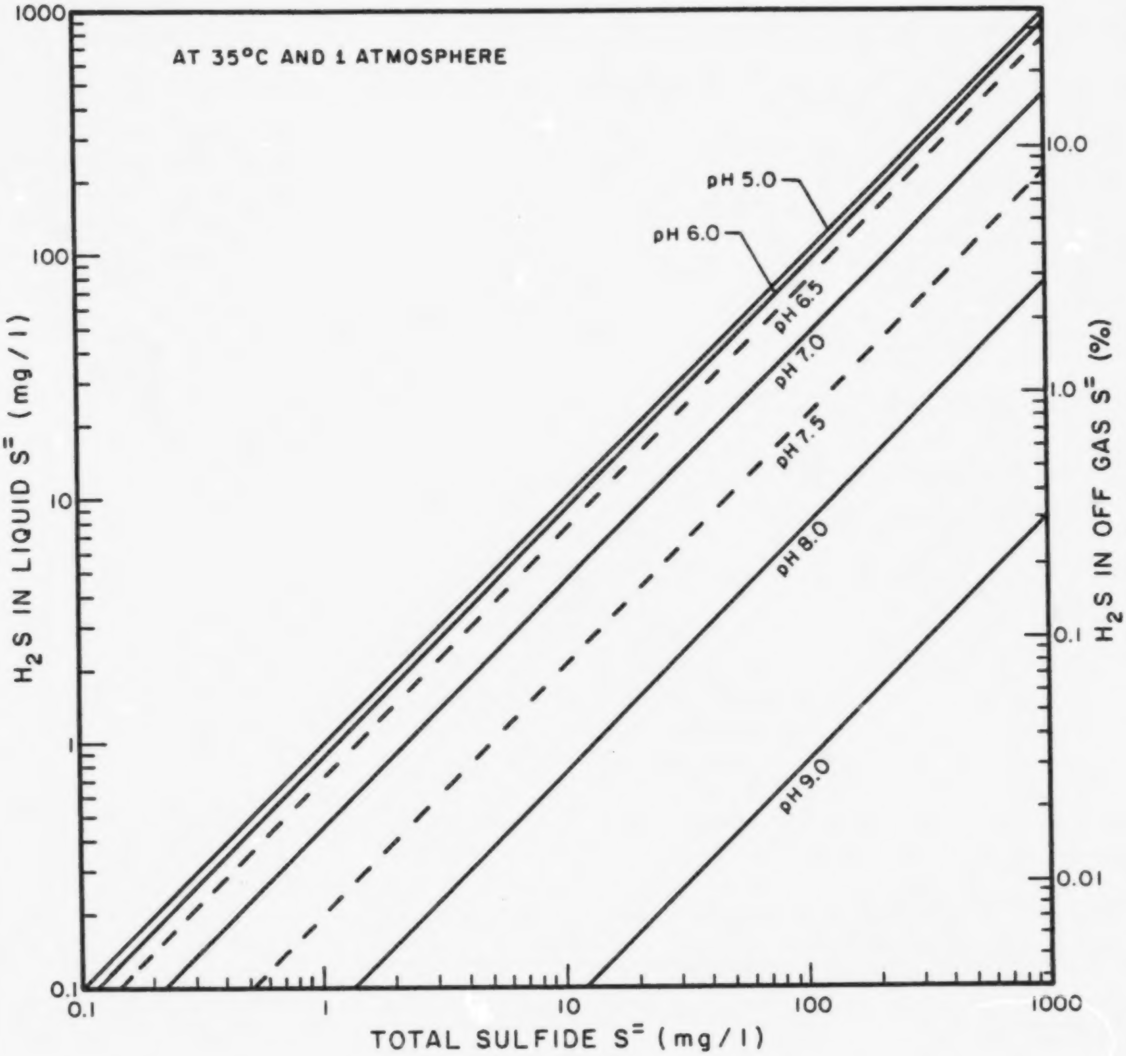


Figure 8-16. Stoichiometric relationship between total sulfide and hydrogen sulfide.

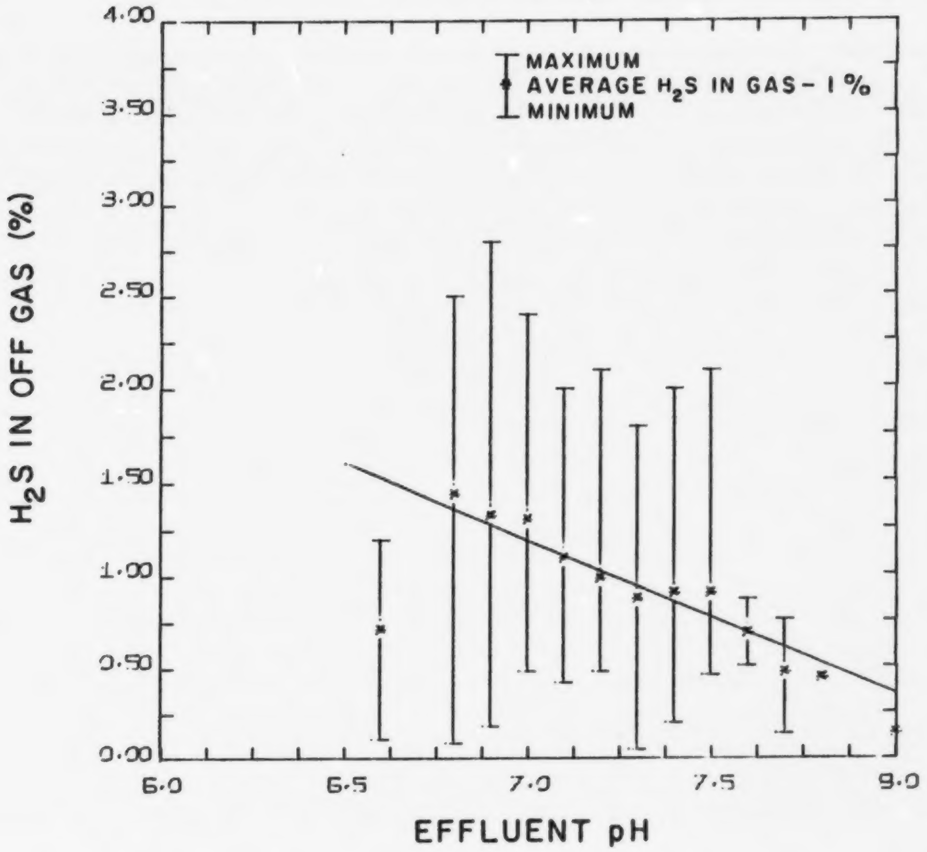


Figure 8-17. Calculated hydrogen sulfide-pH relationships.

Table 8-11 compares several H_2S measurements in the gas using an MSA gas detector tube with calculated values. The detector tube measurements required extensive gas dilution and therefore may not be precise. The measured values generally were higher than the calculated values.

TABLE 8-11. HYDROGEN SULFIDE MEASUREMENT IN ANAEROBIC REACTOR GAS

Unit and Day	Total Sulfide Concentration mg/l H_2S as S	pH	Temperature °C	Measured[a] H_2S in Gas Percent	Calculated H_2S Gas in Percent at 35° and 1 Atmospheric
Filter					
Day 194	46	7.3	36.2	1.41	0.51
199	68	7.3	36.8	0.94	0.76
201	78	7.1	36.2	1.30	1.18
206	68	7.1	36.8	1.18	1.03
Upflow Bed					
Day 194	65	7.3	35	1.18	0.72
199	63	7.5	34.4	0.94	0.49
201	50	7.3	35.6	1.20	0.56
Fluidized Bed					
Day 194	46	7.3	36	1.06	0.51
201	62	6.9	35	1.13	1.25
199	77	5.9	35	4.47	2.67
206	102	6.8	36.5	1.93	2.2
			Average:	2.88	1.52

[a] Measured by MSA Tube.

SOLIDS CLARIFICATION OF EFFLUENTS

Relatively high suspended solids concentrations were observed in the effluent from the units particularly during the early part of the study. Clarifiers were used to settle solids in the effluents from the filter and upflow bed units, and return them to the reactor to increase the rate of reactor capacity development, and in the case of the upflow bed unit, to maintain its removal capacity.

A clarifier was used on the upflow bed unit from day 27 to 60 and from day 83 to 203. A clarifier was used on the filter effluent from day 27 to 60, 83 to 105, 112 to 145 and 180 to 185. Graduated cylinder settling tests were conducted on the effluents from the three pilot plants on day 48 and results are shown in Table 8-12. Solids in suspension decreased rapidly within the first 5 to 10 minutes, and very little settling of solids occurred after 20 minutes for the filter and upflow bed effluents. The effluent solids from the fluidized bed settled very poorly; however, after day 55 effluent solids during good pilot plant operation were generally less than 200 mg/l from this unit.

TABLE 8-12. SETTLING DATA-PILOT PLANT EFFLUENTS

Time (minutes)	Samples - Suspended Solids mg/l			
	Filter	Upflow Bed	Fluidized Bed	Upflow Bed[a]
0	1284	4152	1880	1460
5	1436	-	2080	670
10	635	670	1750	490
20	400	555	1420	456
40	395	430	1500	296
80	310	435	1330	220

[a] June 8, 1983 - Day 152.

60 cm Clarifier Performance on Upflow Bed Effluent:

Clarifier Influent Suspended Solids	2120 mg/l
Effluent Suspended Solids	196 mg/l
Percent Removal	90.8%
Clarifier Settled Sludge Concentration	38,200 mg/l
Volatile Solids Concentration	21,900 mg/l
Percent Volatile Solids	57.3%

Upflow Bed Bottom Sample:

Suspended Solids Concentration	31,600 mg/l
Volatile Suspended Solids	16,200 mg/l
Percent Volatile	51%

A second settling test was run on day 152 on the upflow unit effluent. Similar results of rapid settling in the first 5 to 10 minutes occurred, with gradual settling after 20 minutes. Data taken on the larger clarifier installed on day 150 on the upflow bed effluent, also shown in Table 8-12, indicated the clarifier was removing 90 percent of the solids in the upflow bed effluent.

Figure 8-18 shows data on suspended solids removal by the effluent clarifiers on the filter and upflow bed during the later part of the study. As can be seen very little solids (approximately 13 percent) were removable by settling from the filter effluent; however, external settling of the upflow bed effluent was quite effective, with an average removal of 76 percent. Obviously, the internal clarifier in the upflow bed unit which provided a settling volume somewhat less than the external clarifier, did not perform as had been anticipated.

SIMPLIFIED KINETIC ANALYSIS OF FLUIDIZED BED REACTOR

Introduction

A significant quantity of data was obtained on the fluidized bed system over the study period encompassing a wide range of reactor loading rates, biological solids concentrations and effluent concentrations. The collection of detailed data to allow an in-depth kinetic analysis of the system was not an objective of the study. The data available, however, provided an opportunity to obtain a better understanding of system performance, as related to biological solids growth rate and biological solids and substrate concentrations. An approach to evaluating the fluidized bed reactor kinetics is presented, and can be used as a basis for future studies in which experimental conditions are specifically planned for a kinetic analysis of the fluidized bed reactor.

For the purposes of the analyses conducted on the data, the COD and volatile acid loadings in this section are based on actual liquid volume in the reactor bed. The sand media occupied about 14.6 liters of volume until days 186 and 189 when relatively inert media at the bottom was removed. From day 190 to 207, the sand media occupied about 9.7 liters of reactor volume. Each 100 cm of reactor height contained 18.2 liters of total volume.

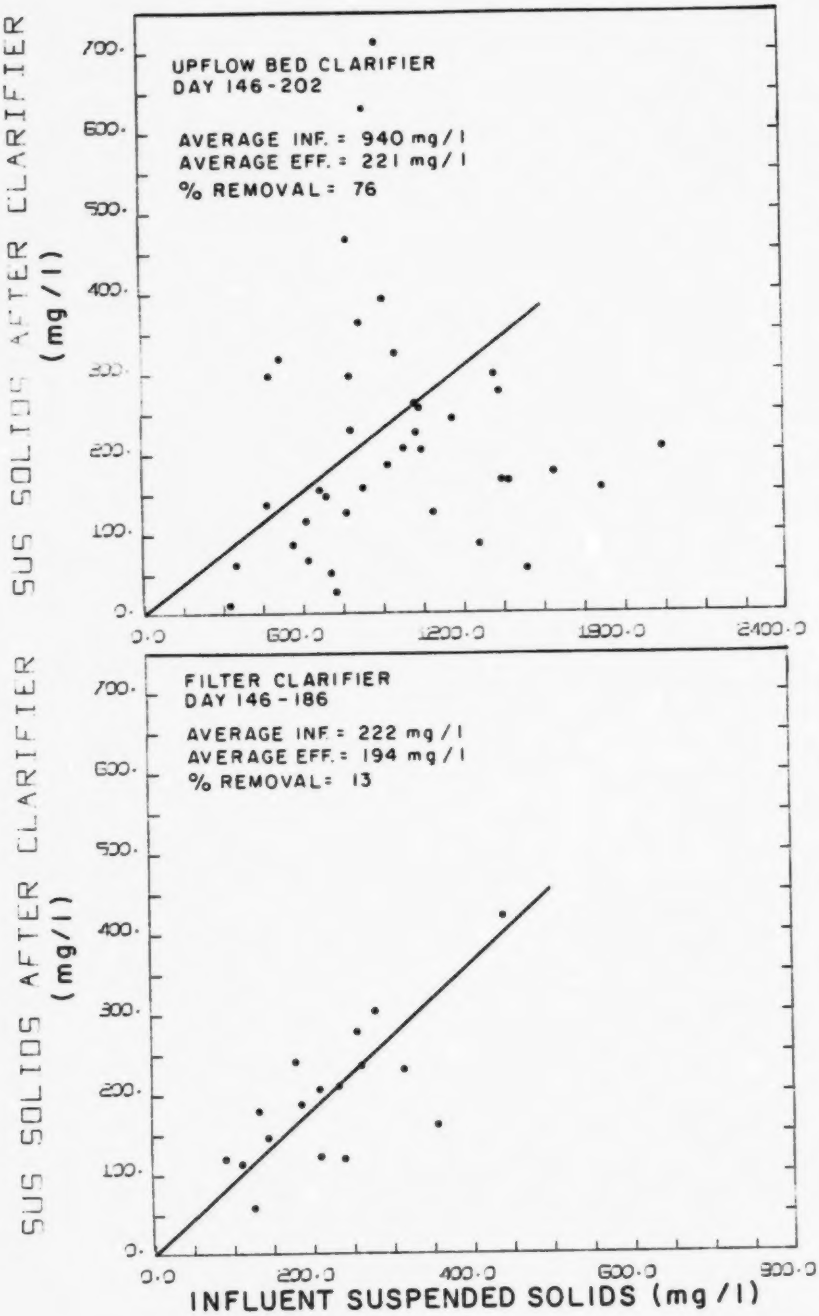


Figure 8-18. Pilot plant effluent solids clarification.

Theory

Completely Mixed Reactor Analysis. The fluidized bed reactor had an extremely high recycle ratio ($N = Q_R/Q_i$) varying from 12,000 initially to 35 at the peak loading rates. Although significant gradients in biological solids concentration exist within the fluidized bed, the average substrate concentration in the reactor is very close to the effluent concentration due to the high recycle ratio. This allows the reactor to be analyzed as a completely mixed system, Figure 8-19, using the total biological mass of solids in the fluidized bed, X, with the total liquid volume in the bed, V_1.

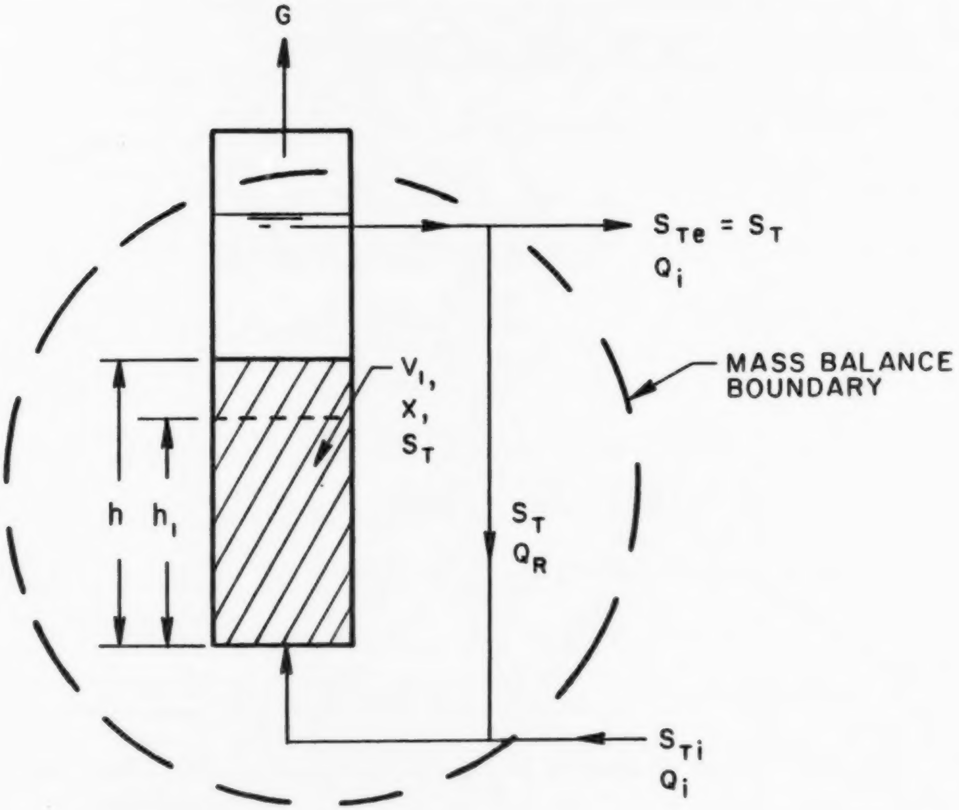


Figure 8-19. Fluidized bed reactor schematic for completely mixed system analysis.

S_T = Soluble COD concentration in reactor
V_1 = Liquid volume in bed
X = Total mass of biological (volatile) solids in bed
h = Fluidized bed height
h_1 = Sludge sand interface
Q_i = Influent flow
Q_R = Recycle flow
G = Gas
S_{Ti} = Soluble COD concentration in influent flow
R_T = Rate of COD removal per unit volume per unit time

A mass balance for the total soluble COD concentration in the liquid phase of the reactor yields:

$$\underline{\text{Rate of Mass}}$$

$$\underline{\text{In}} \quad - \quad \underline{\text{Out}} \quad - \quad \underline{\text{Reaction}} \quad = \quad \underline{\text{Accumulation}}$$

$$Q_i S_{Ti} \quad - \quad Q_i S_T \quad - \quad R_T V_1 \quad = \quad V_1 dS_T/dt$$

At steady state, $dS_T/dt = 0$, the reaction rate occurring in the bed liquid volume is:

$$R_T = \frac{Q_i \, (S_{Ti} - S_T)}{V_1} \tag{2}$$

Defining the overall hydraulic detention time of the influent waste in the bed based on the raw wastewater flow rate as $t_o = V_1/Q_i$ gives:

$$R_T = \frac{S_{Ti} - S_T}{t_o} \tag{3}$$

which is the basic equation defining the total soluble COD removal rate, R_T, in a completely mixed system. Although, within the bed, there is stratification of volatile suspended solids in the sludge layers in the reactor bed, for simplification purposes, the bed is assumed to be a completely mixed zone.

Two Stage Anaerobic Reaction. The two stage reaction has historically(4) been viewed as complex organic COD, S_c, being initially converted to simple volatile acids, S_v. These are then converted to methane and carbon dioxide with subsequent biological growth of both volatile acid formers, X_c, and methane formers, X_v. Written in simplified form, the two stage reaction is:

$$S_c \rightarrow S_v + X_c \qquad \text{(1st Stage)}$$

$$S_v \rightarrow CH_4 + CO_2 + X_v \qquad \text{(2nd Stage)}$$

The total soluble COD measurements (S_T) are comprised of both complex and volatile acid COD (S_{vc}):

$$S_T = S_c + S_{vc}$$

Since volatile acids are also independently measured in terms of acetic acid, volatile acid COD can be determined as follows:

$$CH_3\ COOH + 2O_2 \rightarrow 2CO_2 + 2H_2O$$

Molecular weight ratio basis:

$$\frac{S_{vc}}{S_v} = \frac{64}{60} = 1.067$$

The complex COD can then be determined from measured values as:

$$S_c = S_T - 1.067\ S_v \qquad (4)$$

This allows determination of the complex COD removal rate for the completely mixed reactor to be given in terms of measured values as:

$$R_c = \frac{S_{ci} - S_c}{t_o} = \frac{S_{Ti} - S_T - 1.067\ (S_{vi} - S_v)}{t_o} \qquad (5)$$

To quantitatively determine the volatile acid removal rate, the net biological growth rate occurring in the first stage reaction, R_{xc}, must be estimated. The "net" growth rate is equal to the actual growth rate in the reactor less the rate of biological decay.

If the biological decay rate is assumed to be zero, the upper limit of R_{xc} is obtained as a function of the yield coefficient, Y_c,

$$R_{xc} = R_c\ Y_c \text{ (no biological decay)}$$

For this simplified kinetic analysis, the value of R_{xc} was taken as one half the maximum value. Using a yield coefficient for solids for the complex COD organism of $Y_c = 0.12$ (60), the following equation is developed:

$$R_{xc} = \frac{1}{2}\ R_c\ (0.12) = 0.06\ R_c \qquad (6)$$

For an organism composition of $C_5H_7O_2N$, the COD equivalent of the organism growth rate is 1.42 R_{xc}. The volatile acids production rate in the first stage, R_{v1}, may then be estimated from the first stage reaction as:

$$R_c = 1.067\ R_{v1} + 1.42\ R_{xc}$$

and solving for R_{v1} yields:

$$R_{v1} = \frac{R_c - 0.06\ (1.42)\ R}{1.067} = 0.86\ R_c \qquad (7)$$

The overall volatile acid removal rate in the reactor, R_v, can be determined as the sum of: (a) the measured difference between influent and effluent volatile acids concentrations, and (b) that produced in the reactor from the first stage complex COD degradation:

$$R_v = \frac{S_{vi} - S_v}{t_o} + 0.86\ R_c \tag{8}$$

The upper (no biological decay) and lower (biological decay rate = growth rate) limits for the complex COD coefficient in the above vary from 0.78 to 0.94 or ± nine percent of the average value. Since the majority of the raw waste COD in this study is due to volatile acids, the effect of this variation on R_v is small, within one to five percent.

Kinetic Analysis. The objective of a kinetic analysis is to obtain the removal rate as a function of both substrate and biological solids concentrations. Since the major portion of the COD in the raw wastewater was volatile acids, major emphasis was placed on this constituent. The kinetic analysis involved analysis of two phases: (a) the initial log growth phase of the methane formers occurring in the reactor at relatively high substrate concentrations, and (b) the majority of the data after significant growth had occurred and both substrate and biological solids concentrations appeared to affect removal rate (Michaelis Phase).

Initial log growth phase of methane formers. In the log growth phase of the microbial growth cycle, biological growth is assumed to occur only as a function of biological solids concentration and not substrate concentration (zero order kinetics with respect to substrate) as given by:

$$R_{xv} = \frac{dX_v}{dt} = \mu_v X_v$$

where μ_v is the maximum "net" (growth-decay) growth rate of methane formers (X_v). Integrating the above over a given time interval

$$\int_{X_{vo}}^{X_v} \frac{dX_v}{X_v} = \mu_v \int_{t_o}^{t} dt$$

yields:

$$X_v = X_{vo}\, e^{\mu_v(t - t_o)}$$

Since the biological decay rate is relatively small compared to the growth rate at high substrate concentrations, the volatile acids removal rate can then be related to the biological growth rate using the yield coefficient as:

$$R_v = \frac{R_{xv}}{Y_v} = \frac{\mu_v}{Y_v} X_{vo}\, e^{\mu_v(t - t_o)} = k_v X_{vo}\, e^{\mu_v(t - t_o)}$$

or taking the natural log of both sides to linearize the above:

$$\ln R_v = \ln (k_v X_{vo}) - \mu_v t_o + \mu_v t \qquad (9)$$

Determining μ_v as the slope of a semilog plot of R_v versus time allows the estimation of the maximum reaction rate coefficient for volatile acids as:

$$k_v = \mu_v / Y_v = \mu_v / 0.05 = 20\ \mu_v \qquad (10)$$

where a value of $Y_v = 0.05$ is used.(5)

Michaelis Phase. During the major portion of the study on the fluidized bed reactor, the rate of substrate removal, R, appeared to be affected by both substrate, S, and biological (volatile) solids, X_v, concentrations. Michaelis kinetics were used to analyze for this effect using:

$$R = \frac{k\, S\, X_v}{S + K_s} \qquad (11)$$

where K_s, the Michaelis constant, is the substrate concentration at which the reaction rate is one half the maximum. The initial log growth phase given previously is a special case of the Michaelis kinetics where $S >> K_s$.

There are a number of ways to linearize the above equation, the most common being:

$$\frac{1}{R_x} = \frac{1}{k} + \frac{K_s}{k\ S} \tag{12}$$

where R_x is the substrate removal rate per unit volatile suspended solids concentration (R/X_v). Both k and K_s can be determined from linear regression analysis or from the intercept and slope of a plot of $1/R_x$ versus $1/S$.

Results

Log Growth Phase. Figure 8-20 shows data available from the fluidized bed reactor for the kinetic analysis. The volatile acids removal rate calculated from Equation 8, shows an increase of about two orders of magnitude over the course of the study. Note that the removal rate is based on reactor liquid volume, total reactor volume less volume occupied by sand media. The variability occurring in this removal rate is due to either rapid changes in COD loading rate or short term reactor upsets.

The biological solids content of the reactor increases with time as growth is retained. A significant gradient in X_v concentration with depth existed in the reactor after the initial startup period with the major portion of the lighter volatile solids occurring in the upper portion of the reactor. The total volatile solids concentration, X, in the reactor was calculated as the sum of all taps, of the product of volatile solids concentration measured on each tap sample, and the liquid volume associated with the tap. No continuous curve was drawn through the chronological plot of solids data due to periodic significant solids losses during plant upsets.

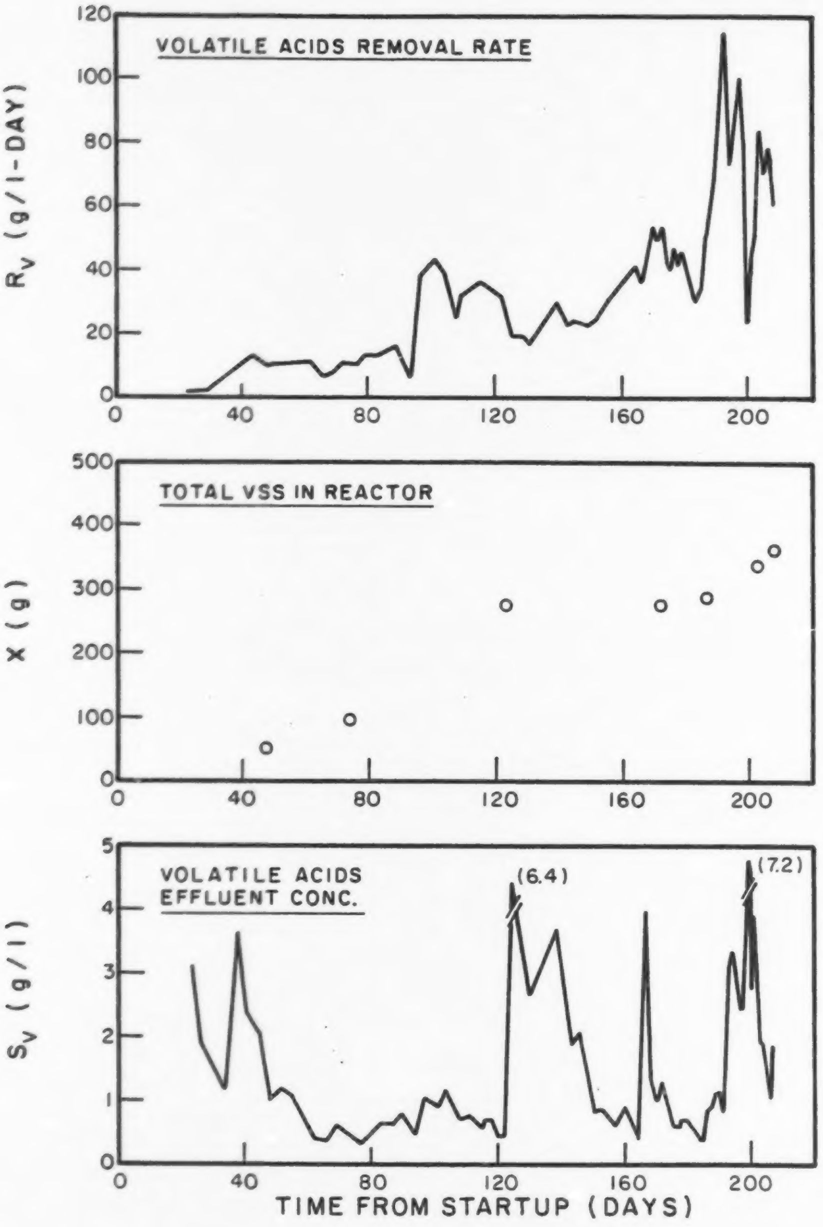


Figure 8-20. Chronological data volatile acids, volatile acids removal rate and volatile suspended solids.

The peak volatile acids concentrations on Figure 8-20 on days 125 and 199 were due to plant upset with significant biological solids loss. Both of these upsets were due to stripping of the solids from the media by gas inadvertently injected in the recycle flow. The first period was due to air injection during a sand trap draining operation. Approximately 25 days were required for reactor recovery. This long period was probably due to subjection of the anaerobic organisms to aerobic conditions. The last upset period was due to foam entrapped in the recycle flow during the highest loading period. The reactor had remained anaerobic during this period and significant recovery occurred after a few days, to about 75 percent of the prior peak removal rate. The high volatile acids concentration on days 38 and 167 were dynamic responses of the reactor to significant load changes.

The initial log growth phase of the reactor was evaluated using the data up to day 45 when the volatile solids held in the reactor were relatively low, volatile acids were above 1100 mg/l and reaction rate increased an order of magnitude over this short time period. As shown by the dashed line on Figure 8-21 the COD loading rate was increased over an order of magnitude during this short period, allowing the reaction rate to geometrically increase. This high rate of change in COD loading was discontinued on day 38 as the volatile acids concentration approached 4000 mg/l. At no other time in the study was the loading rate increased tenfold in a one week period.

From Equation 6, the slope of the removal rate plot on Figure 8-21 provides the maximum "net" growth rate of the methane formers as 0.31/day. This value can be compared to the value of 0.44/day given by Lawrence and McCarty,(6) for an acetic acid substrate. The difference of 0.13/day is probably due to biological decay (0.04/day) and partial substrate limitation at the effluent volatile acid levels.

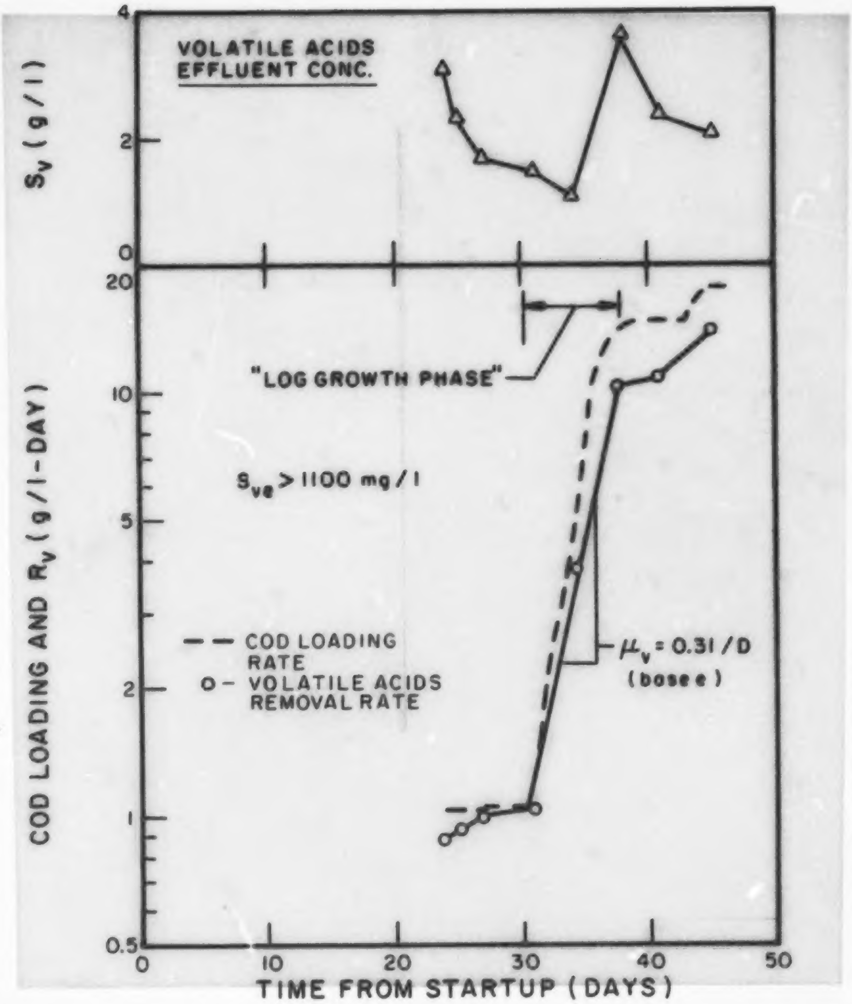


Figure 8-21. COD loading and volatile acids removal rates during startup period.

A similar analysis was conducted on the data collected during the latter stages of the study at the highest COD loading rates as shown on Figure 8-22. Following a relatively steady loading period of 45 to 65 g/l-day from day 170 to 180, the raw waste flow was discontinued for three days and the reactor operated only on recycle due to lack of waste condensate. The reactor was then increased in loading rate from 34 to 150

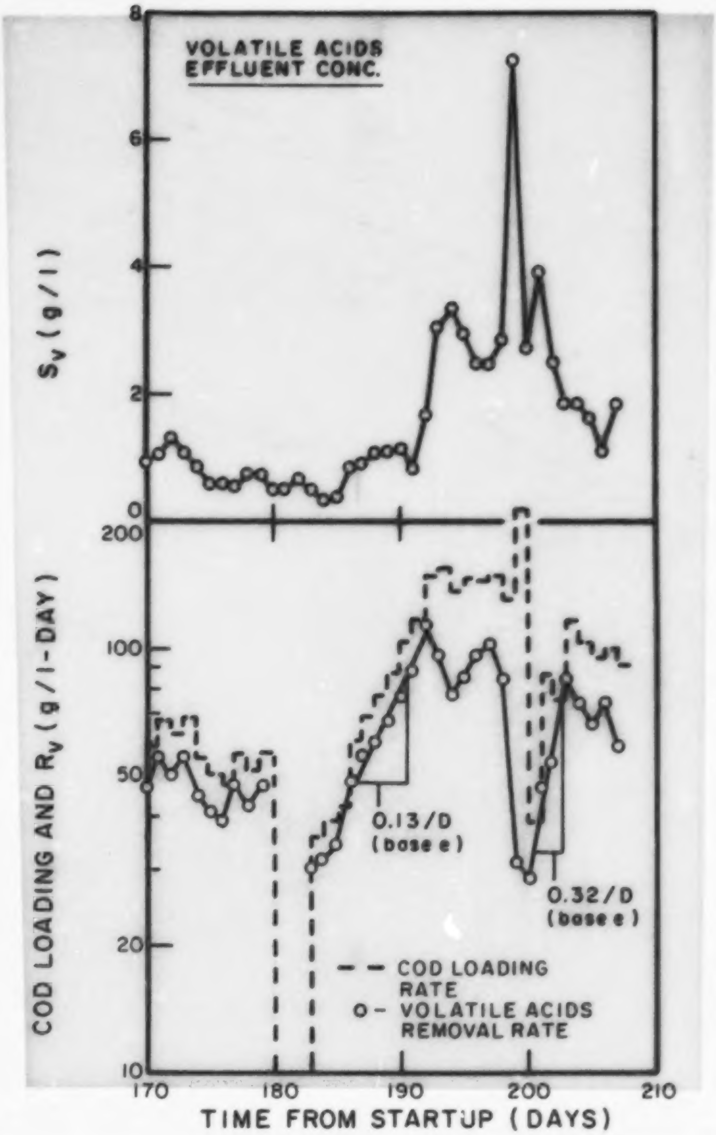


Figure 8-22. COD loading and volatile acids removal rates during final high growth phases.

g/l-day with a similar increase in removal rates to day 192. The slope of the removal rate plot yields an overall growth rate of 0.13/day, significantly lower than that calculated during the initial phase of the study;

thus indicating substrate limitation on growth rate. The reactor volatile acids concentration averaged about 1000 mg/l during this period. Following this period for six days (day 193 to 198), removal rate varied between 78 and 96 g/l-day, although loading rate was significantly greater and volatile acids concentrations were above 2400 mg/l. This suggests that the biological solids loss was equal to or greater than the net growth during this period.

Following the second major upset on day 199, a significant increase in reaction rate again occurred from day 200 to 203 with volatile acid concentrations above 1900 mg/l. The log growth phase yielded a growth rate of 0.32/day similar to that obtained during the initial phase. This indicates that the prior upset was not toxic to the methane formers allowing the remaining organisms to grow at their maximum potential rate. The relatively constant to slightly declining removal rate from day 203 to 207, suggests that the solids loss equals, or slightly exceeds growth rate. Effluent suspended solids averaged 236 mg/l during this period and were significantly higher than the 90 mg/l average from day 145 to 180, during which time the bed volume increased from 31 to 40 liters. In the above analysis the large change in volatile acids concentration between days 198 and 200 required the accumulation term in Equation 1 be included in the calculation of removal rates for this period. This effect was negligible for all other periods.

The marked increase in removal rate during this second upset period was significantly different than the relatively constant removal rate after the first upset following day 125. This can be attributed to the different nature of the upsets, the first having a toxic reaction on the methane formers due to aerobic conditions, while the second was a nontoxic washout of a portion of the biological growth.

Michaelis Phase. To evaluate the data during relatively stable conditions using Michaelis kinetics, the biological solids concentration existing in the reactor had to be estimated for each day of the study. The only continuous data available to accomplish this was data on bed height as shown on Figure 8-23. The fluidized bed expanded during growth periods, while it decreased after upsets. At days 186 and 189 sand was removed from the bottom tap to remove inert media from the reactor; thus, decreasing the height of sand (h_1) and overall bed height (h). Prior to day 187, the quantity of sand held in the reactor was substantially constant allowing a correlation between reactor biological solids and bed height to be obtained as shown on Figure 8-24. A linear correlation between total volatile solids held in the reactor and bed height existed from bed heights between 151 to 195 cm. The total solids held in the reactor then began to increase much more slowly with increased bed height to 230 cm. After sand removal,

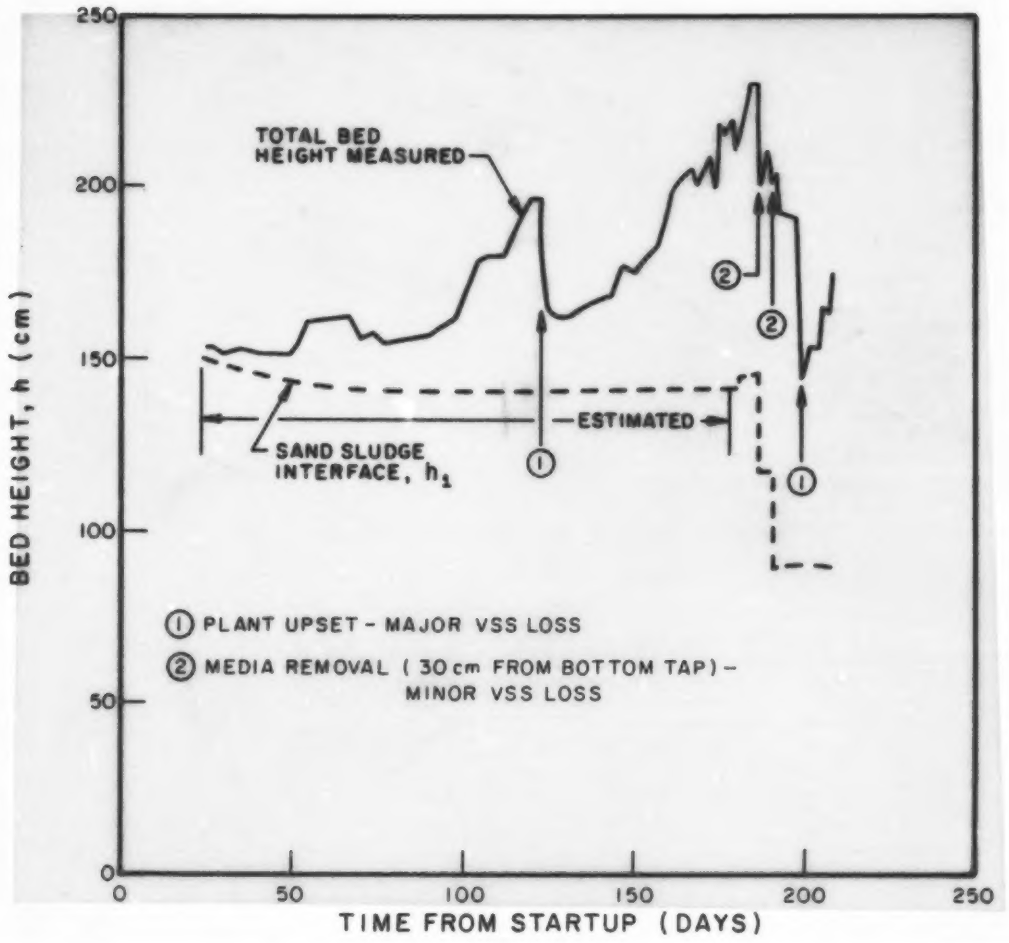


Figure 8-23. Fluidized bed height over study period.

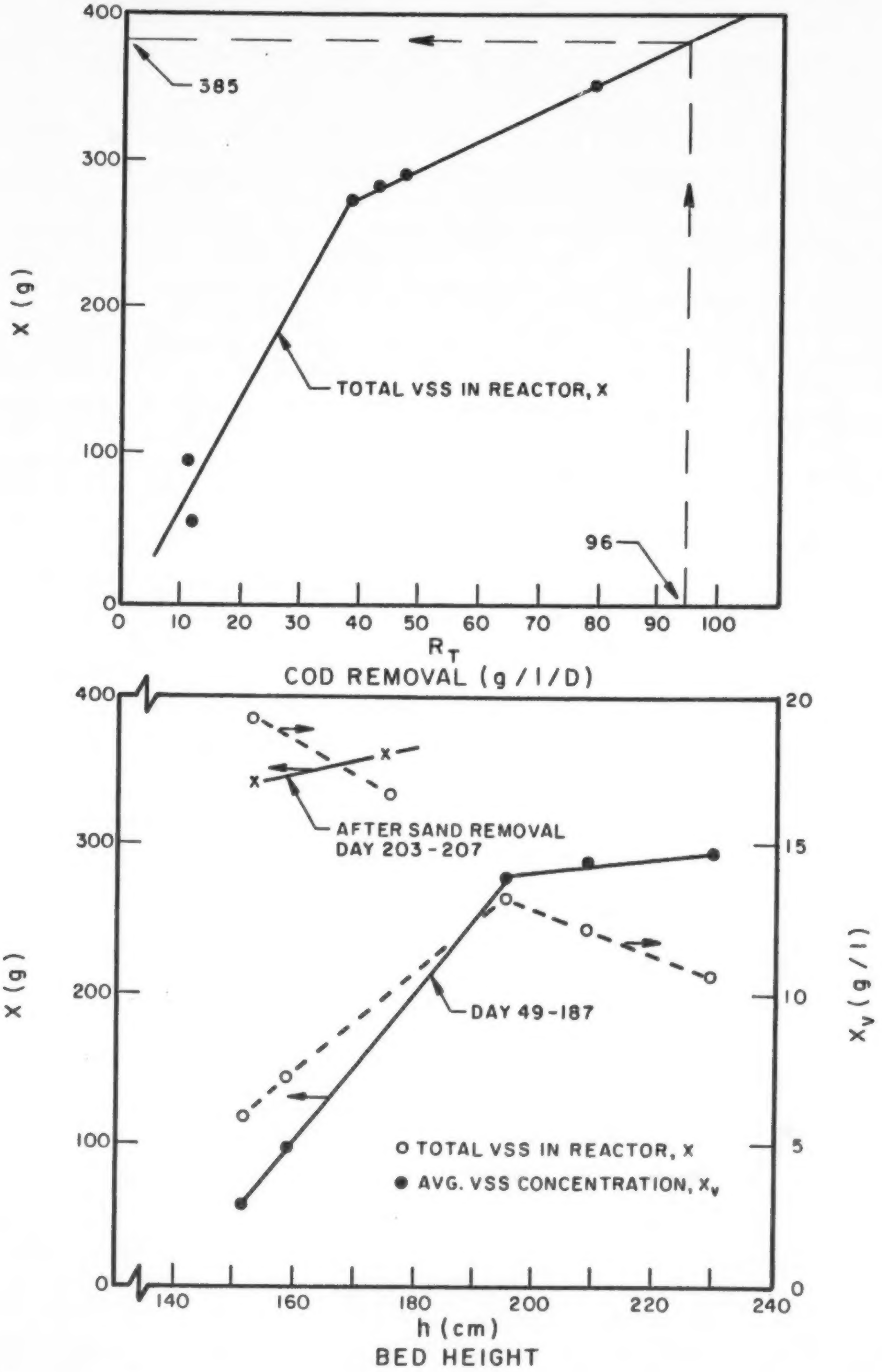


Figure 8-24. Volatile solids in fluidized bed versus COD removal and bed height.

total bed height decreased below 180 cm but total solids measured on days 203 and 207 were significantly higher due to the very high growth period at the end of the study. For the Michaelis analysis to day 187, and from days 203 to 207, the bed height correlation on Figure 8-24 was used to obtain the total volatile solids content in the reactor for each day analyzed.

During the peak removal period, from day 193 to 198, the biological solids held in the reactor was assumed to be constant at 385 grams as estimated from the COD removal rate correlation on Figure 8-24. The upset periods from day 125 to 153 and from day 199 to 202 were deleted from the analysis, due to the inability to estimate volatile solids during the latter upset, and the nature of the first upset, probably changing the organism distribution in the reactor. The initial startup period to day 70 was also deleted from the analysis as were days 94, 167, and 183 to 192 due to significant load changes.

The results of the Michaelis analysis for volatile acids are shown on Figure 8-25. A linear regression plot through the data indicates that 49 percent of the variability in removal rate can be explained by the effect of volatile acid effluent concentration. This correlation is quite good considering the biological solids estimates that had to be made in conducting the analysis. A similar analysis conducted on total soluble COD yielded a correlation (r^2) of 37 percent, and on complex soluble COD of 8 percent. From results of the regression analysis the maximum reaction rate and Michaelis constant with the 95 percent confidence limits are given in Table 8-13. The value of 5.8/day for k_v is not greatly different from the value of 6.2/day obtained from the log growth analysis using data excluded from the Michaelis analysis. The Michaelis value of 5.8/day would be somewhat greater (10 to 30 precent) if based on only the methane formers and not total biological solids. Lawrence and McCarty,(6) have reported a Michaelis value for volatile acids of 165 mg/l at 35 degrees C. The higher value of 610 mg/l obtained in this study, may be due to the fixed film nature of the biological solids on the media causing an additional diffusional resistance and an increase in the apparent Michaelis value.

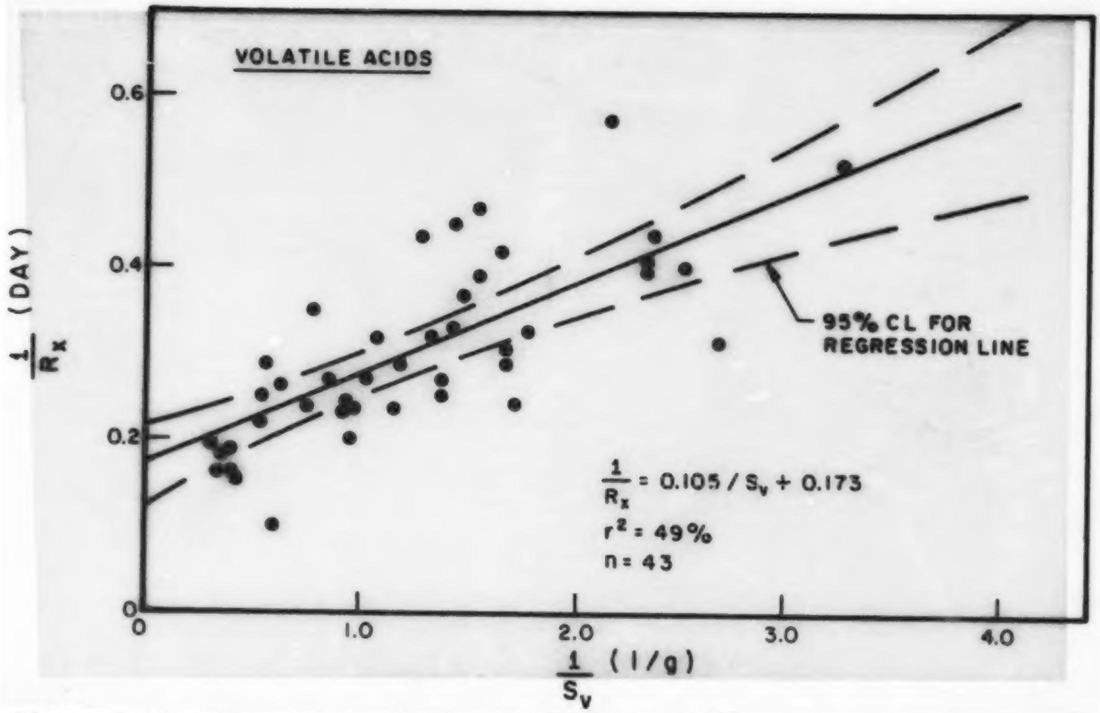


Figure 8-25. Michaelis analysis of volatile acids.

TABLE 8-13. MICHAELIS RESULTS FOR FLUIDIZED BED DATA

Substrate	Reaction Rate Coefficient k, day^{-1} Value	95 Percent C.L.	Michaelis Constant K_s, mg/l Value	95 Percent C.L.
Volatile Acids	5.8	4.6 to 7.9	610	420 to 800
Total Soluble COD	6.5	4.8 to 10.0	1200	710 to 1700
Complex Soluble COD	1.3	1.0 to 1.8	150	-12 to 300

Figure 8-26 shows the total COD removal rate per unit volatile suspended solids as a function of the total soluble COD concentration showing both the calculated Michaelis line and observed data. The data is a three to five day average value during relatively constant loading and

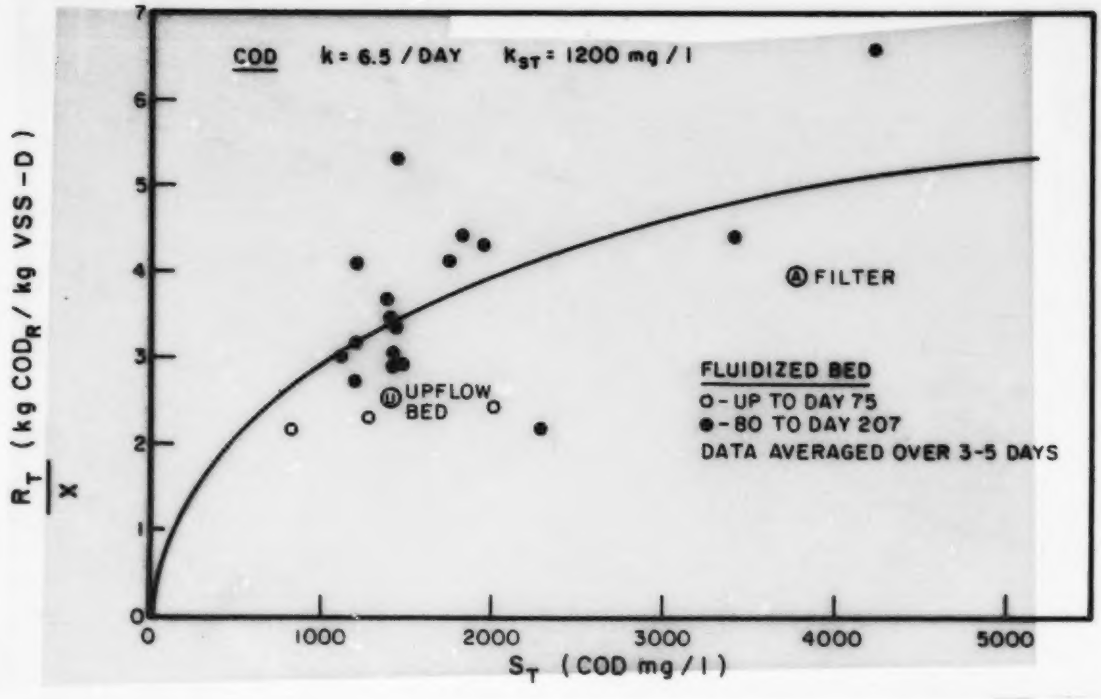


Figure 8-26. Michaelis kinetics summary for total COD data.

removal periods. The upflow bed and anaerobic filter data were obtained at the end of the study. The latter two systems have unit removal rates somewhat lower than the line of best fit for the fluidized bed data, but well within the scatter (95 percent confidence limits) of the fluidized bed data. Thus, no significant difference in unit removal rates exists for the three systems. The unit removal rates prior to day 75 were also lower than the line of best fit presumably due to the fluidized bed reactor being still in the growth development phase.

The "k" rate for the total soluble COD is somewhat greater than that for volatile acids while the Michaelis value is almost double. This latter difference may be due to slowly degradeable or refractive COD present in the effluent.

The complex COD data fit poorly (2 to 8 percent) to Michaelis kinetics due to the low complex COD concentration (15 to 35 percent of the total COD) in the wastewater. The lower "k" rate based on total biological solids, indicates that the major fraction of the biological solids are methane formers and not volatile acid formers, due to the high volatile acids concentration in the raw wastewater.

Summary

The simplified kinetic analysis provides a rational basis for understanding the anaerobic fluidized bed system. It is apparent that the fluidized bed reactor is a continual growth reactor with rapid accumulation of biological solids up to some limit. Attempting to obtain steady state effluent data at various COD loading rates, when growth is well below the maximum, provides no significant kinetic information, since a relatively constant effluent concentration will result due to changes in biological growth. The technique of using a geometric increase in the COD loading rate near the methane former maximum growth rate, while maintaining an upper level on volatile acids concentrations, will bring the reactor to a given design condition in the shortest possible time.

The simplified Michaelis analysis of the fluidized bed data yields maximum methane former growth rates somewhat similar (within 25 percent) to suspended growth systems. However, the Michaelis constant, K_s, is significantly greater than reported for suspended growth systems requiring relatively high volatile acid concentrations to maintain high reaction rates, e.g., 2500 mg/l for 80 percent of maximum rate.

SECTION 9

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